THE DETERIORATION OF LUBRICATING OILS

by

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Being a thesis presented to the University of Glasgow for the degree of Doctor of Philosophy.

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W.K.A. Aitken

Glasgow 1958.

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INTRODUCTION

Lubricants in use today are normally prepared from refined mineral oil fractions, and in service these oils have to withstand severe conditions of temperature and pressure.

Despite the many advances in refining techniques and the use of additives, the life of an oil is still limited. In the course of duty it may become contaminated with dust, water and metal fragments rendering it less efficient as a lubricant. More important than this, however, is deterioration due to oxidation. This changes the characteristics of the oil and results in the production of such undesireable products as sludge, lacquer and acids.

Unfortunately, the conditions under which lubricating oils are required to operate are precisely those which promote oxidation. Splashing of oil and resultant intimate contact with air is a feature of most engines. The principles on which internal combustion and compression ignition engines operate necessitate the air for combustion coming into contact with thin films of oil. Since high temperatures are an essential characteristic of all engines, the bulk of the oil

is always at a fairly high temperature, and due to sliding motion high temperatures are momentarily developed at points where the oil is in thin films.

As engine design advances and new principles of motivation, such as the gas turbine, are introduced, the above factors increase in magnitude and lubricating oils are required to withstand even more stringent conditions.

Nature of Lubricating Oils

Mineral lubricating oils are derived from crude petroleum which is, apart from a low percentage of impurities, a complex mixture of hydrocarbons. The number of individual hydrocarbons is great and the transition in properties so gradual that it is impossible, other than with low molecular weight material, to separate individual components by the orthodox physical and chemical methods. Inference has, however, given an accurate concept of the nature of petroleum.

It has been shown that petroleum mixtures can be divided into three groups viz:

I) Paraffins, or saturated hydrocarbons with straight or branched chains.

II) Napthenes, saturated cyclic hydrocarbons of one or more rings which may have paraffin side chains.

III) Aromatics, hydrocarbons containing one or more aromatic nuclei, which may have napthene rings and/or paraffin side chains.

In addition a number of other factors peculiar to hydrocarbons in petroleum have been established.

These include:

(a) Paraffins present are mostly straight chains. There are very few isoparaffins;

(b) Molecules containing aromatic rings without napthene rings are rare;

(c) When there is more than one aromatic ring these are condensed;

(d) Asphaltic material consists mainly of polycyclic aromatics;

(e) Aromatic rings generally have short paraffin side chains, napthene rings long side chains;

(f) There may be up to five rings per molecule.

The proportion of different hydrocarbons present in crude petroleum varies widely from field to field and this inevitably decides what may be derived from it. Fractions with viscosities greater than 50 seconds Saybolt at 100°F are used in the preparation of lubricating oils and are termed "Lubricating oil distillate". Separation of the distillate from the crude oil is carried out in a number of refining processes, distillation being the first of them. This removes low molecular weight components and may also be used to separate high boiling and asphaltic material.

A secondary function of distillation is to divide the lubricating constituent into narrower boiling range fractions. The temperature required to distil all but the lighter lubricating oils at atmospheric pressure would lead to considerable thermal cracking and, consequently, the operation is normally done under vacuum.

When it is desired to recover a heavy "bright stock", lost on the removal of asphaltic material from an oil by distillation, the resinous and asphaltic material is removed by solvent precipitation. In this process oil is mixed with a suitable solvent, such as propane under pressure, and two layers separate. When stripped of solvent the lower layer gives the precipitated solvent, the upper layer the oil and any wax present.

The removal of excess aromatics from a lubricating fraction is done by extraction with a suitable polar solvent. Such solvents as sulphur dioxide, furfural and phenol when mixed with an oil give two phases. The upper phase, or "raffinate", contains the required paraffinic and naphthenic constituents plus a little solvent, the lower phase, or "extract" contains the bulk of the solvent and the aromatics. Removal of the solvent by distillation yields an aromatic residue and the required oil.

Wax is precipitated from lubricating oil by chilling and removed by filtration. A suitable solvent, in which wax is insoluble, is often incorporated to facilitate filtration.

Two other common refining techniques employed are sulphuric acid treatment and adsorption on a suitable solid such as clay or Fuller's earth. The former removes the same type of material as solvent extraction, which has largely replaced it. The latter improves clarity and colour by removal of compounds of a polar nature such as phenols.

The fractions of different viscosity obtained from the refining processes are blended in calculated proportion to give lubricating oils of a required viscosity. Depending on the use to which the oil is to be put additives may be incorporated in it.

Analysis of Mineral Oil

Investigation into the deterioration of lubricating oils requires as much as possible to be known about the starting material. Owing to the impossibility of separation into individual components it has long been established that a complete molecular analysis is impossible. A large number of empirical and semi-analytical methods have however been proposed. Van Nes and van Westen give details of these. (1)

The most informative and unambiguous method to date, for assessing mineral oil, has proved to be Structural Group Analysis. Here the hypothetical mean molecule in the fraction is considered and the distribution of the carbon atoms among the three types of hydrocarbon groups present given; i.e. the percentage of the carbon atoms in paraffinic, naphthenic and aromatic structure. Also given are the number of naphthenic and aromatic rings per mean molecule.

The classical method of structural group analysis is the "direct" method, all other forms being evolved from this. The method is based on theoretical consideration of the mathematics of hydrocarbon molecules.

A paraffin molecule of a given molecular weight will have a definite and deducible percentage of hydrogen. With the introduction of naphthene rings into this molecule each one added results in the loss of two hydrogen atoms. Any saturated molecule containing naphthene rings will, therefore, have a lower hydrogen content than the paraffin of the same molecular weight. It is possible to establish a direct relationship between hydrogen content, molecular weight and the number of rings per molecule in a saturated hydrocarbon, viz:

$$R_n = 1+(8.326-0.5793H)M/100$$

where R_n is the number of naphthenic rings per molecule

H is the percentage of hydrogen

M is the molecular weight.

In the case of a molecule containing aromatic rings, when these are hydrogenated to saturated rings, each aromatic carbon atom adds a hydrogen atom. The hydrogen taken up in the hydrogenation of double bonds is thus a measure of the number of aromatic rings present and an equation for this can be derived. The analysis of the resulting saturated molecule can be completed as above, except that the percentage hydrogen is now a measure of the total rings present in the original molecule. The difference between total rings and aromatic rings gives naphthenic rings. From the picture of the hypothetical mean molecule so obtained the carbon distribution can be calculated.

The experimental technique of the direct method for structural group analysis consists of carefully controlled hydrogenation followed by an accurate measurement of the hydrogen content in the saturated molecule.

Certain assumptions require to be made regarding the material to be analysed by structural group analysis. Such factors as whether naphthene rings are five or six membered and whether rings are condensed or not affect the theory and equations derived therefrom.

The first published method of structural group analysis was due to Vlugter, Waterman and van Westen, and is known as "Waterman Ring Analysis" (2). Additivity is a feature of hydrocarbon molecules and the authors noted that the Lorentz-Lorenz specific refraction

$$r = \frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$$

where n = refractive index at 20 C using the sodium - D - line and d = density at 20 C

is additive for increments of C and H. Hence "r" is proportional to the percentage hydrogen in the hydrocarbon molecule. Measurement of specific refraction and molecular weight in a saturated oil sample thus gives the number of rings per molecule.

For the analysis of samples containing aromatic rings the same workers gave a method using aniline point (2). The aniline point for the sample under examination was measured. This was compared with the corresponding value for the completely hydrogenated sample of the same molecular weight and specific refraction as the original sample, obtained from a graph. The difference in the two aniline points was then, by means of suitable factors, employed to give the percentage of aromatic rings and to predict what the specific refraction of the sample would be were it completely hydrogenated.

The Waterman ring analysis which dispensed with the difficult measurements of the direct method was refined by Leenderste to give the "density method" (1). This dispensed with the measurement of aniline point. Instead the aromatic content and the specific refraction of the completely hydrogenated sample were estimated from the difference between the density of the sample and the density of the completely hydrogenated oil of the same molecular weight and specific refraction as the original sample. The latter factor was obtained, as with aniline point, from a curve.

At this stage analysis was reduced to the measurement of refractive index, density and molecular weight. During attempts to simplify the density method equations for obtaining carbon distribution and ring content were evolved in terms of the above quantities which eliminated the need for calculating the specific refraction. These equations are the basis of the n-d-M method of structural group analysis (1) described in detail later.

A more recent publication gives a method which replaces the measurement of molecular weight by the measurement of kinematic viscosity. The method is due to Boelhouwer and Waterman and known as the V_K-n-d method (3). Details of this method are also given later in this work.

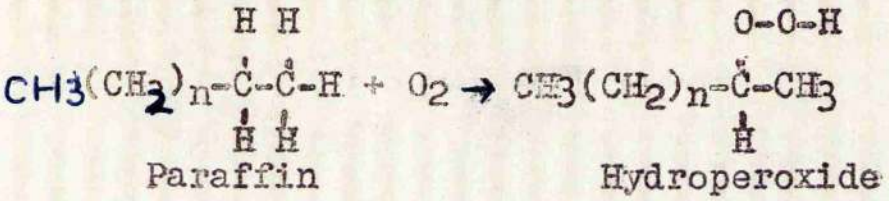
Chemistry of Hydrocarbon Oxidation

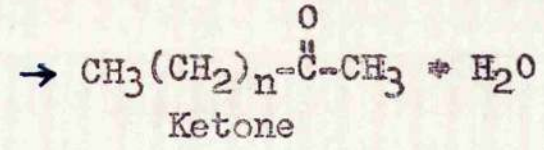
The complex nature of lubricating oil makes it impossible to identify specific products of oxidation except those of low molecular weight including carbon dioxide and water. Since, however, fractions are composed mainly of paraffin, naphthene and aromatic hydrocarbons it is of advantage to consider the oxidation of these. Zuidema (4) has reviewed the work in this field and has postulated possible reaction mechanisms.

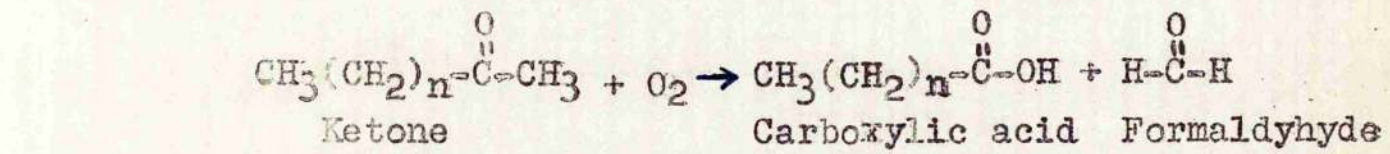
At moderate temperatures (ca. 150°C) oxidation of paraffins has shown the formation of preponderant quantities of ketones as well as a series of acids ranging from formic to those containing one less carbon atom than the original hydrocarbon. These, when considered quantitatively, indicate attack to be centred primarily at the beta carbon atom, with the gamma secondarily involved and so on toward the centre of the molecule. Small quantities of alcohols have also been found.

Water can account for a considerable proportion of the oxygen used in all hydrocarbon oxidations and in the case of paraffins, acids and formaldehyde are also found in the liquid products. Gaseous products contain mainly carbon dioxide with carbon monoxide, hydrogen and saturated hydrocarbons of low molecular weight.

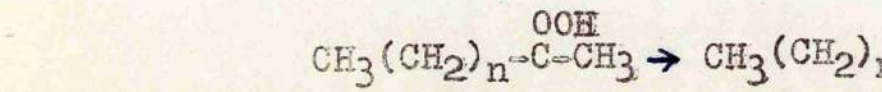
Many studies of all types of hydrocarbon oxidation have shown that the principle products formed in the early stages are hydroperoxides, which later decompose to give the ketones already mentioned. From this Zuidema has postulated the mechanism, in the temperature range considered, to be:

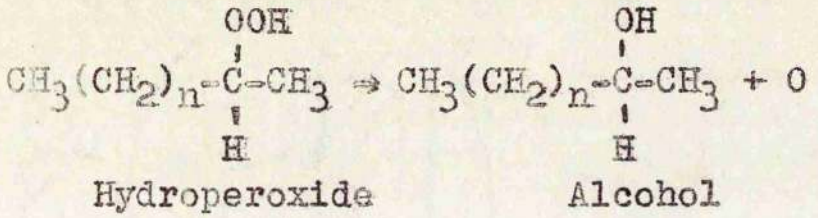






There would also be some molecules where the attack would be at the gamma rather than the beta carbon to give the corresponding ketone. The carboxylic acid would then contain one less carbon atom and acetaldehyde would be split off. The acids may be further oxidised by similar mechanisms at other carbon atoms and the aldehydes are probably oxidised to the corresponding acids and to some extent to carbon dioxide and water. The formation of alcohols is believed to be the result of the reduction of the peroxide.





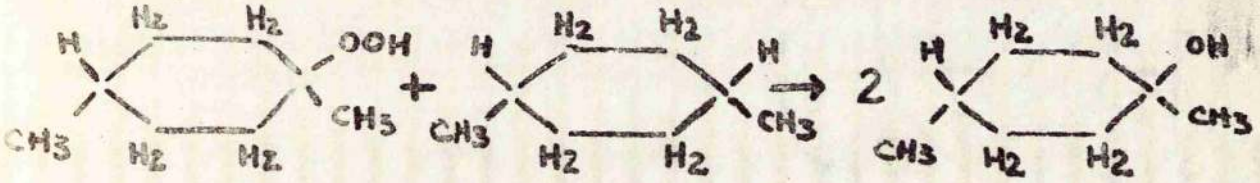
Esters could be formed by condensation of an acid and an alcohol.

Chavanne and Bode (5) have made an extensive study of the oxidation of 1,4-dimethylcyclohexane and Dupont and Chavanne (6) studied the oxidation of cyclopentane derivatives. Zuidema cites these as typical C_6 and C_5 naphthenic hydrocarbon oxidations.

The principle oxidation product of 1,4-dimethylcyclohexane was 1,4-dimethylcyclohexanol. Other products included water, carbon dioxide, β-methyl-δ-acetylvaleric acid, acetic acid, β-methylvaleric acid, dimethylcyclohexanediol and acetonylacetone as well as small amounts of hydrogen, carbon monoxide, methane, ethane and formic acid. The postulated mechanism for the reaction is attack at the tertiary carbon atom to form the peroxide, as with the paraffin.

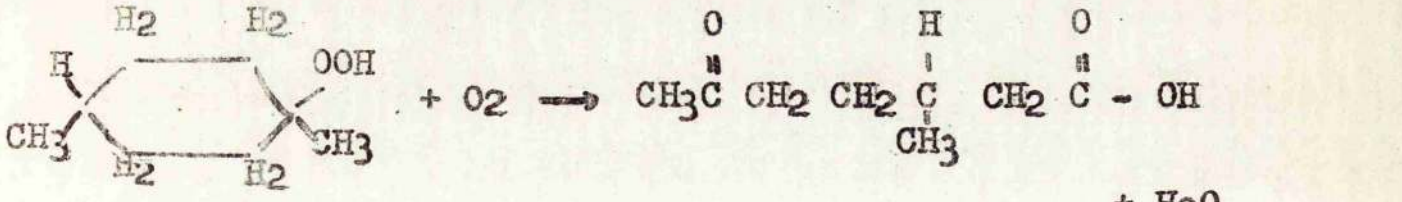
1, 4 - dimethylcyclohexane Hydroperoxide of 1, 4 - dimethyl-cyclohexane

The peroxide then decomposes by reduction to give the alcohol.



In the case of the paraffins the formation of the alcohol was a secondary reaction; for this material it is the main one. The formation of the diol can be similarly explained.

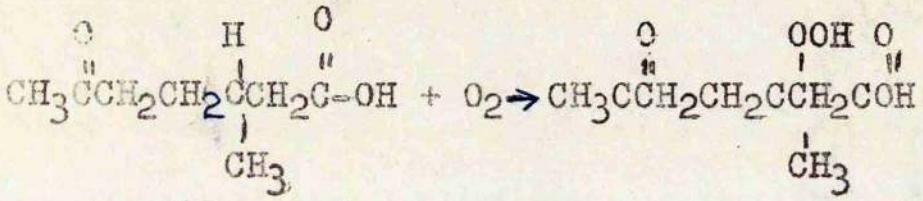
The other oxidation products require the rupture of the naphthene ring which takes place when the peroxide is further oxidised.



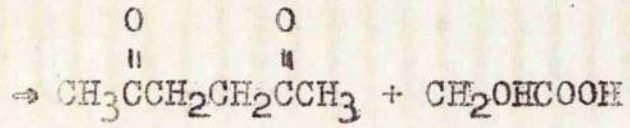
Hydroperoxide of 1, 4 - dimethylcyclohexane

β- Methyl - δ acetylvaleric acid

This differs from a paraffin in that it is the hydroperoxide itself which is oxidised and not the ketone. Also the product can have the same number of carbon atoms as the original hydrocarbon. Acetonylacetone formation may be explained by further attack of the molecule at the other tertiary carbon, which appears to be the vulnerable part of the naphthene ring as follows:

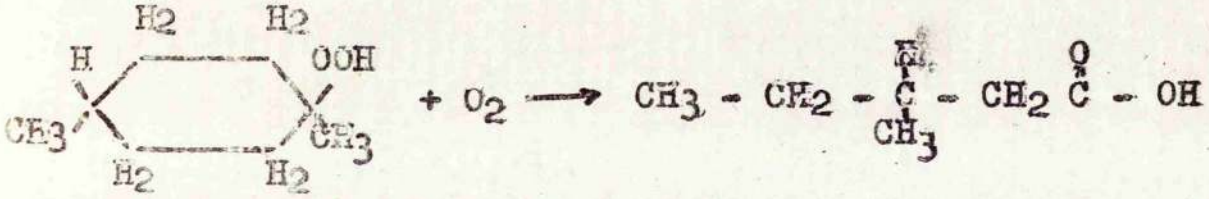


δ-methyl-ε-acetylvaleric acid Hydroperoxide of δ-methyl-ε-acetylvaleric acid



Acetonylacetone Glycolic acid

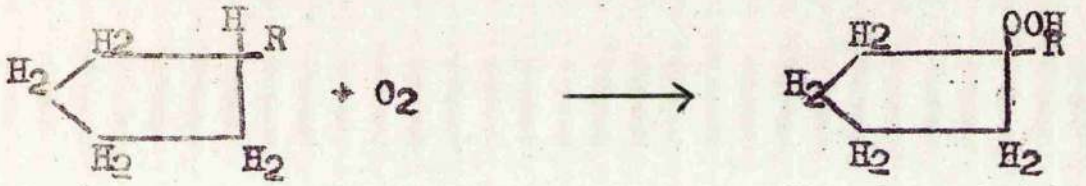
Glycolic acid was not reported in the oxidation and Zuidema assumes it to be oxidised to simpler products such as formic acid, carbon dioxide and water. The formation of δ-methylvaleric acid is explained by the oxidation of the hydroperoxide with a split in the naphthene ring thus:



Hydroperoxide of 1, 4 - Dimethylcyclohexane δ - Methylvaleric acid + CH_3COOH acetic acid

The formation of hydrogen, methane, and ethane, present in very small quantities, is assumed to be due to cracking.

The oxidation of two n-alkyl cyclopentanes, ethyl and butyl, already referred to, produced ketones of the same number of carbon atoms as the original hydrocarbon. This is believed to be due to the reduction of the hydroperoxide formed at the tertiary carbon atom and in this way differs from the cyclohexane derivative which formed an alcohol initially.

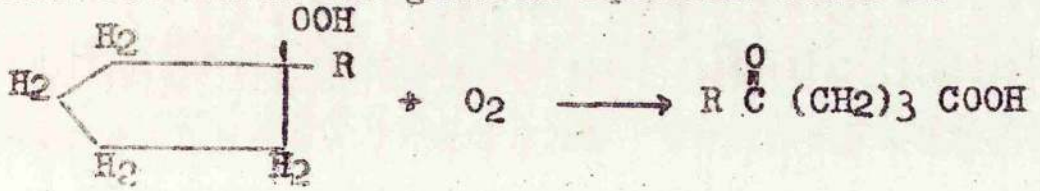


Alkyl cyclopentane

Hydroperoxide of alkyl cyclopentane

$\longrightarrow$ CH - CH CH CH C - R + O alkyl butyl ketone

Also formed were keto derivatives of heptanaic and nonanaic acids for which the general equation would be



Lower molecular weight acids were also produced as products of further oxidation.

The reason for the difference between C5 and C6 naphthenes is not clear but may have been due to there being two tertiary groups in one and only one in the other molecule, or to the difference in size of either ring or side chains or possibly to different conditions of oxidation.

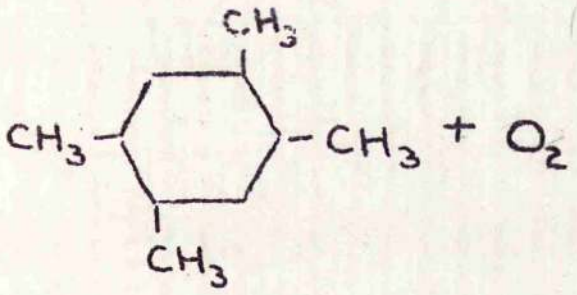
Notwithstanding, the two illustrations show what may happen on oxidation of naphthene and gives some general principles regarding the mechanism.

The work of Stevens (7) and Stevens and Roduta (8) on the oxidation of benzene derivatives can be used to postulate the mechanism of aromatic hydrocarbon oxidation. Oxidations at moderate temperatures have shown attack by oxygen to be always centred about a carbon atom attached to the benzine ring to give aldehydes in the case of methyl benzenes and ketones in the case of substituted benzenes containing one or more alkyl groups larger than methyl. When the carbon atom attached to the benzene ring is a tertiary carbon the ketone contains the smaller of the other two groups attached to the carbon atom, the remaining one splitting off to give a low molecular weight acid. This has also been found to be the case if one of these groups is a phenyl group. No matter whether an aldehyde or ketone is formed the mechanism is essentially the same: the formation of a C = O carbonyly group at the vulnerable carbon in the molecule. Acids resulting from the further oxidation of aldehydes and ketones are also obtained.

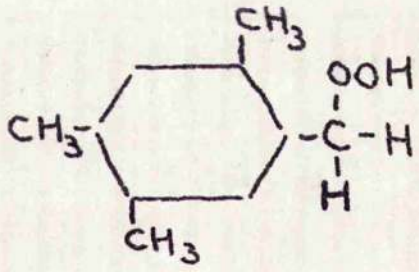
Although no peroxides have been reported it is assumed that the initiating stage in aromatic hydrocarbon oxidation is the formation of a hydroperoxide group at the carbon atom

attached to the benzene ring. The peroxide then decomposes either by dehydration to give an aldehyde or ketone, or by loss of a molecule of alcohol, later oxidised to an acid, to form a ketone, depending on whether the starting material contains a methyl group, an alkyl group or is a tertiary carbon atom.

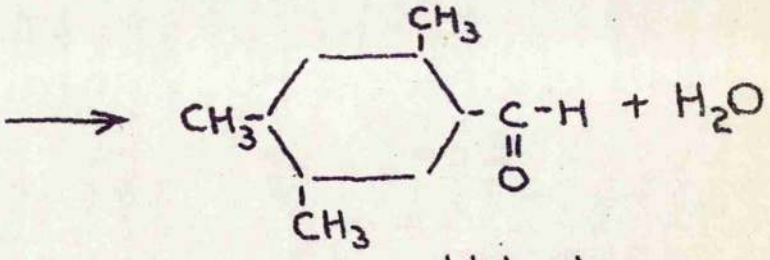
Taking durene as a typical methyl benzene the mechanism of oxidation is given as



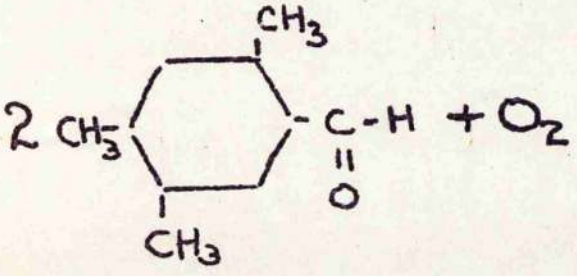
Durene



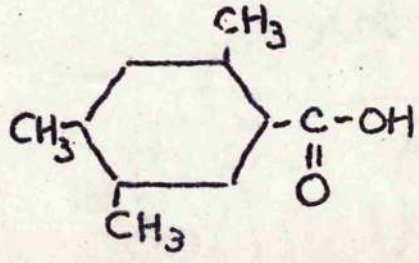
Hydroperoxide



Durylic aldehyde

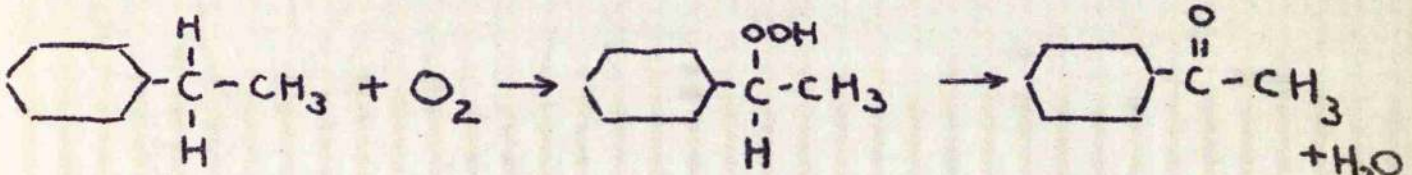


Durylic aldehyde

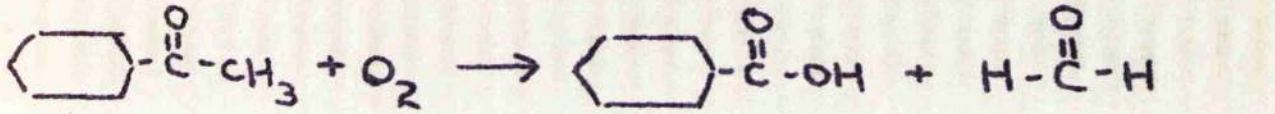


Durylic acid

Ethyl benzene can be taken as an example of the oxidation of an alkyl benzene and the mechanism is postulated thus:



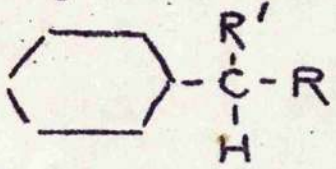
Ethyl benzene Hydroperoxide Acetophenone



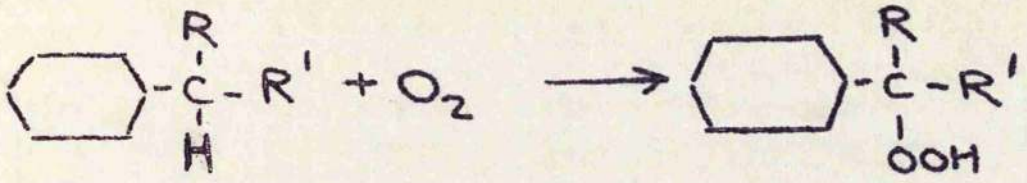
Acetophenone Benzoic acid Formaldehyde

Formaldehyde Formic acid

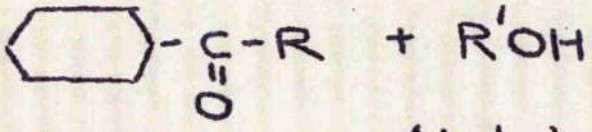
If R and R^1 represent H or alkyl groups or if one of them is a phenyl group in the following structure



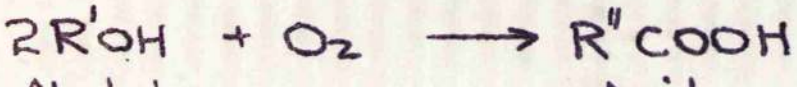
where R and R^1 may be the same but when they are not if R is regarded as the smaller group, general equations applicable to the above hydrocarbon oxidations and also applying to the case where the carbon atom attached to the benzene ring is a tertiary carbon may be represented as follows



Hydrocarbon Hydroperoxide



Ketone Alcohol or water



Alcohol Acid

tert-Butylbenzene cannot form a hydroperoxide at the carbon atom adjacent to the benzene ring since it is a quatenary carbon. This would explain the fact this compound is known to be very stable under oxidising conditions.

In comparison to naphthenes no rupture of the ring structure takes place during the normal oxidation of aromatic hydrocarbons and oxidation always results in the production of dark insoluble condensation products.

When oxidation of complex lubricating oil fractions, containing large numbers of hydrocarbons is carried out it is only possible, in the case of the bulk of the products formed, to obtain functional groups. Work done has shown the above mentioned products to be found in varying percentages, the relative amounts and nature of these depending on the starting material. Moreover, one type of hydrocarbon is known to influence the attack on another.

Dornte (9) and Denison (10) both report preponderant quantities of peroxides when white oil is oxidised. For the same material Dornte found the products formed, in terms of the percentage of the oxygen absorbed in each, in order of magnitude to be, peroxide, carbonyl, water and acid. Considering the works of Dornte (9), Fenske et al (11) and Hicks-Bruun et al (12) lubricating oils can be expected on the average to give 40% of the oxygen absorbed as water and between 3 and 10% as carbon dioxide.

It has long been established that oxidation of high aromatic oils gives high percentages of asphaltenes, and consequently refining processes have been partly directed towards removal of these by solvent extraction.

These asphaltenes are analogous to the dark insoluble products referred to in the oxidation of pure aromatic hydrocarbons and Larsen et al (13) in the oxidation of a lubricating oil progressively extracted to remove aromatics and report that less aromatic samples give less asphaltenes, more water and less carbon dioxide.

Zuidema (14) comparing available data, points out that the distribution of absorbed oxygen, among the products, in the oxidation of a lubricating oil resembles that of a pure

alkylnaphthalene oxidation and states that this class of compound may be the one bearing the brunt of the attack by oxygen in the complex mixture of hydrocarbons in lubricating oil.

Rates of Oxidation

The physical properties of an oil after oxidation are dependent on the nature of the products formed and also on the amounts present, determined by the rates at which they are produced. The kinetics of the oxidation of pure hydrocarbons, mixtures and lubricating oil fractions has been studied by a number of workers. Rate kinetics can be indicated by the absorption curve, showing the volume of oxygen absorbed, by a fixed weight of sample, plotted to a base of time. Stabilities can be shown by the time required for a fixed weight to absorb a predetermined volume of oxygen. Dornte et al (9, 15, 16), Larsen, Thorpe and Armfield (17), Fenske et al (11), von Fuchs and Diamond (18), Balsbough and Oncley (19) and Hock and Lang (20) report investigations of this nature. Chernozhukov and Krein (21) describe an alternative method whereby they oxidised samples in a bomb under pressure and took the saponification number as a measure of the extent of oxidation.

Zuidema (14) has co-ordinated the available data on oxidation rates and stabilities from which it is possible to

indicate general trends. Work on pure hydrocarbons generally considers those compounds whose molecule is either a paraffin a naphthene, an olefin, a benzene or naphthalene aromatic or a combination of these. Paraffins, naphthenes and alkyl naphthenes have been found to have intermediate stabilities. The least stable compounds are those containing olefinic double bonds, benzene rings with alkyl side chains and partially hydrogenated naphthalenes. Naphthalene derivatives on the other hand have been shown to be the most stable of the hydrocarbons with naphthalene itself the most stable of all. It has in fact been shown that compounds containing a polyaromatic nucleus are extremely stable.

The extreme stability of naphthalene, aromatics compared to the benzene homologs is considered by Larsen, Thorpe and Armfield (17) to be due to the difference in the oxidation products as inhibitors, naphthols on the one hand, phenols on the other. This they justified by adding some preoxidised α-methylnaphthalene to n-amylbenzene which when oxidised gave a similar absorption rate curve to the former.

When the double bonds of olefins and alkyl benzenes are hydrogenated to the corresponding paraffins and alkyl cyclohexanes it is found that there are increases in the stabilities to oxidation.

On the ohter hand when naphthalene is hydrogenated there is a marked loss of stability; so much so that tetralin is the least stable hydrocarbon to oxidation known. Complete hydrogentation to decalin results in an increase in stability again but with a value still considerably less than the original naphthalene.

Long alkyl side chains in cyclic hydrocarbon molecules reduce the stability. Molecules containing a stable group such as a naphthalene, and an unstable one such as an olefinic bond give intermediate stabilities.

The rates of oxidation of isomeric hydrocarbons depend on the positions of the different groups within the molecules. The results of Larsen, Thorpe and Armfield (17) show that in the oxidation of primary, secondary and tertiary amylbenzene the order of increasing stability is as given. This is in line with the reaction mechanisms proposed. The primary derivative on oxidation forms the hydroperoxide at the carbon atom adjacent to the benzene ring, which dehydrates to the ketone. In the case of the secondary derivative the hydroperoxide will be formed as before but since there is no second hydrogen on the carbon adjacent to the benzene ring the ketone will be formed and alcohol split off. This involves the splitting of a C - C bond whereas the former does not. In the case of tertiary amylbenzene no hydroperoxide can be formed at the carbon adjacent to the benzene ring.

In the oxidation of mixtures of hydrocarbons of different stabilities the rate obtained is not an intermediate stability. The mixture may in fact be considerably more stable than any of the components. There appears to be interaction between the various molecules.

The aromatic content of a mixture of hydrocarbons has been found to be significant in oxidation rates. According to von Fuchs and Diamond (18), Fenske et al (11) and others, there is an optimum aromaticity (in the region of five to ten percent) giving maximum stability.

The effects of Lubricating Oil Oxidation

The oxidation of a lubricating oil causes a number of changes in its properties normally detrimental to engine operation. Thus the oil can be said to have deteriorated. In the laboratory deterioration is seen as a darkening in colour, an increase in viscosity, the ability for solid and semi-solid material to settle out and an increase in the value given by a carbon residue test. In engines it has a number of effects leading to inefficient running and a shortening of engine life.

Bearing Corrosion

Bearing corrosion results from the solution of bearing metal by acids. This in turn leads to metal failure and contamination of oil.

The problem has been made more serious by the replacement of the formerly used corrosion resistant babbit metals by alloys required to withstand the temperature and load conditions of modern engines. Many of these alloys contain the chemically reactive cadmium. The acids causing corrosion are not only those produced on oxidation of the lubricating oil but also aqueous acids formed on combustion of the fuel.

The mechanism of bearing corrosion by oil solutions of organic acids has been shown to differ from the normal dissolution of a metal by an aqueous acid in that an oxidising agent must also be present. The action of this may be to form the oxide of the metal, which is in turn dissolved by the acid, or to prevent polarisation by oxidising the hydrogen to water. Denison (10) has shown that the peroxides formed act as oxidising agents. In the early stages of an oil oxidation when the peroxide content was high and the acidity low a lead test strip became coated with an oxide film which was later dissolved when acids were formed. Again, an oil high in peroxides and low in acidity was found to be much more corrosive than one high in acidity but free of peroxides.

Other workers have shown molecular oxygen to be an oxidising agent promoting corrosion but it is only effective at relatively low temperatures when its solubility is appreciable.

A number of factors influence the rate at which oil oxidation may cause bearing corrosion. Different acids give different corrosion rates. The relative amounts of acids and peroxides formed in relation to other products will cause oils of equal stability to differ in corrosive effect. Certain constituents in the oil or products formed during oxidation may cause passivation of bearing surfaces. Temperatures, loads, engine design and fuel used are all factors likely to influence the rate of bearing corrosion.

Sludge and Lacquer

The oxidation of a lubricating oil also creates oxidation products which are insoluble in the bulk of the oil. These appear in two forms, viz., particles which settle out from the oil or "sludge", and hard coatings on engine parts, termed "lacquer". The problem is complicated by dust, water, products of incomplete combustion and oxidation of the fuel, iron oxide from corrosion and wear, etc. which are usually also present.

Oils with high aromatic and sulphur content give the least soluble oxidation products. This is especially true of condensed ring aromatics. The insoluble products are probably esters resulting from the condensation of acids and alcohols. Denis and Clayton (22) suggest that lacquer may be formed by condensation of the oxyacids on hot metalic surfaces.

It has been shown (14) that increasing degrees of extraction of a Californian distillate gave decreasing formation of asphaltenes. Similar results are obtained when quantities of unextracted oil are added to an extracted (aromatic free) one. The fact that lacquer can be formed with a mixture of normal lubricant and an unstable white oil although none forms with white oil alone indicates that the formation of insolubles is not proportional to the instability of oil but depends on the presence of aromatics.

When oil insolubles first form they are colloidal and only when they flocculate is sludge formed. Flocculation depends on the ability or otherwise of the oil to keep "insolubles" in solution or colloidally dispersed. Oils of different composition differ in their dispersant action. Paraffins have poor solubility characteristics for asphaltenes but as the naphthene content increases solubility increases. Increasing aromatics in an oil increases the solubility and the greater the number of aromatic rings the less insoluble settles out. Since paraffinicity is associated with high viscosity index, high viscosity index will result in more asphaltenes coming out of solution.

On oxidation, lubricating oil may form products making it more solvent to colloidally dispersed insolubles. Soluble metal soaps formed by the acid products of oxidation and engine metals have dispersant action.

Increasing the temperature of an oil increases its ability to keep sludge in solution but this leads to increased oxidation.

The field of additives has been given little attention in the present work but certain compounds have dispersant properties and are incorporated in oils. Such additives are known as detergents.

Friction and wear

Two main types of lubrication are encountered where oils are used, namely hydrodynamic and boundary lubrication. A third form, extreme pressure lubrication, is a special type of boundary lubrication. The products of oxidation of lubricating oils have a bearing on all of these.

When two sliding surfaces are spearated by a continuous film of oil the lubrication is hydrodynamic. The laws of hydrodynamics apply to this film and the coefficient of friction is proportional to the dimensionless parameter $\frac{ZN}{P}$, where Z is the oil viscosity, N the relative speed of the two surfaces and P the pressure between them. Hence under constant load and speed conditions friction is proportional to viscosity. Consequently, oxidation has little effect except insofar as the resulting increase in viscosity may increase the coefficient, but this is often offset by dilution by the fuel.

Boundary lubrication exists when the oil film is so thin that the laws of hydrodynamics do not apply and some metal to metal contact exists. The nature of the friction is dependent on the surface properties of the oil and the forces of the metal oil boundary. Oils of the same viscosity may give different coefficients of friction. This property is known as "oiliness".

Little appears to be known about the effects of lubricant oxidation on friction, but polar compounds are formed and since they are surface active agents, they should be capable of reducing boundary friction. Exline, Kramer and Bowman (23) and King (24) have shown that the oxidation of a lubricating oil improves boundary lubrication.

Extreme pressure, or E.P. lubrication, is characterised by high pressures and temperatures, but despite the terminology, it is mainly a high temperature effect. It is encountered chiefly in hypoid gears. As bearing pressure increases, the oil film becomes thin, abraisive wear takes place and the high temperatures generated cause temporary welding and tearing away of the metal. The latter effect is termed "seizure".

Many compounds containing oxygen such as carboxylic acids, esters, ketones and oxidised petroleum fractions, all of which are formed when an oil is oxidised, improve E.P. lubrication but little work appears to have been done on oxidised oils as such. The mechanism by which these compounds act is believed to be chemical. Due to the high temperatures generated reactions

take place with the metal, the products of which prevent seizure and reduce friction. A particular reaction is the formation of soap films with carboxylic acids and metals.

As with lubrication little can be found in the literature on the effect of oil oxidation on wear, except corrosive wear, already dealt with. It is generally recognised, however, that apart from corrosive wear oxidation generally causes a decrease under boundary and E.P. conditions. Since there is no metal to metal contact there is no wear in pure hydrodynamic lubrication.

Oxidation Tests

A number of tests have been devised for predicting the probable behaviour of a lubricating oil when used under oxidising conditions. Some of these measure stability or the extent to which the oil oxidises. Others measure the effects produced due to the existence of products of oxidation in the oil after oxidation has taken place. There are also tests which seek to simulate practival conditions in which the above variables are measured while the oil is in the process of oxidising.

Laboratory tests are used for small scale testing and may give good initial predictions but are limited in their scope. On the larger scale, engine tests which nearer approach true operating characteristics, have been devised.

Oxidation stability of lubricating oils is generally examined by contacting with air or oxygen at elevated temperatures. The method is usually to bubble the gas through the oil.

Many varieties of this method have been proposed but only one has been adopted in this country by the Institute of Petroleum for engine oils. This is the test which originally appeared as the British Air Ministry, or B.A.M., oxidation test for aviation engine oils.

Garner, Kelly and Taylor (25) describe the work they did on the original test concerning the reproducibility of the results and the effects of small changes in the specified constant conditions. Their paper appeared prior to the adoption of the test as a standard by the Institute of Petroleum.

In the test (I.P.48/44) air at the rate of 15 litres per hour is bubbled through 40 ml. of oil in a boiling tube maintained at 200°C for 6 hours. The boiling tube is then removed and allowed to stand at room temperature for 12 to 18 hours. After this time the tube is replaced and blowing continued for a further 6 hours when the tube is removed and allowed to cool.

The extent of the oxidation is determined by comparing the viscosity and carbon residue of the oxidised sample with the corresponding values for the original oil. Kinematic viscosities, at 100°F, for the two samples are expressed as a ratio:

$$\frac{\text{viscosity after oxidation}}{\text{viscosity before oxidation}}$$

The viscosity of an oil generally tends to increase on oxidation and the nearer the ratio tends to unity the less the oil has oxidised under the test conditions. Carbon residue is measured before and after oxidation by the Ramsbottam method and the increase noted. A quantity of the oil is evaporated, in the absence of air, in a glass bulb at 550°C. The amount of residue remaining is expressed as a percentage.

Another test based on the same principle and used to evaluate the oxidation characteristics of lubricating oils is the Indiana oxidation test (26). In this, air at the rate of 10 litres per hour is blown through 300 ml. of oil contained in a glass tube of specified dimensions and maintained at 341°F in an oil bath. At intervals samples are withdrawn and examined for sludge value. This is obtained by diluting with A.S.T.M. precipitation naphtha, filtering and weighing the sludge precipitated. A graph of sludge is drawn to a base of oxidation time and the times required for the formation of (i) 10 mg. sludge per 10 gm. oil and (ii) 100 mg. sludge per 10 gm. oil estimated and taken as the criteria of oxidation. Viscosities may also be measured in this test.

When applied to oils conta ining additives the Indiana test gives results inconsistent with those obtained in practice. The test has accordingly been modified to give the "Indiana stirring oxidation test for lubricating oils" (27). Instead of air blowing the sample is aerated by high speed stirring of the oil. 250 ml. of oil in a 500 ml. beaker maintained at 330°F is stirred with a glass stirrer at 1,300 r.p.m. in the presence of copper and iron catalysts. Sludge and acidity which are measured every 24 hours for a maximum of 72 hours, are taken as the criteria of oxidation.

In the Sligh oxidation test (28), a 10mg. sample of oil is placed in a special glass flask fitted with a ground and clamped stopper. The flask is filled with oxygen and placed in a bath at 200°C for two and a half hours. At the end of this period the flask is cooled and the asphaltic material determined, the number of mg. in the 10 gm. of oil being recorded as the Sligh number.

Another type of stability test in which the oxidising gas is bubbled through the oil sample is carried out with an apparatus first described by Dornte (9) and now common in oil investigation. The gas used is oxygen and the equipment records continuously the absorption of it by the oil. Oxygen bubbles through the oil in a closed circuit. The oil itself is contained in a glass cell kept at a constant high temperature. As the gases, containing lighter products of oxidation, leave the cell they pass through an absorption and condensing system which removes them and may also serve to recover them for examination and estimation. As well as the quantity of oxygen absorbed in a given time the shape of the absorption-time curve is used to characterise the sample.

A number of tests are available for measuring the defects or otherwise of a deteriorated oil. Examples of such determinations are bearing corrision, wear, sludge and lacquer formation, etc.. A few of these measure the required quantity

on an already oxidised oil with no further oxidation taking place during the test. The majority, however, simulate operating conditions by starting with fresh oil progressively being oxidised during the test period.

The Existant Corrosivity or E.C. test (29) is an example of a test in which no appreciable oxidation takes place during the test. This is a bearing corrosion test, the principle of which consists in exposing a specimen of bearing metal, prepared under specified conditions and weighed on an analytical balance, to the oil at the conditions of the test. In the E.C. test the specimen is immersed in 20 gms. of oil at 156°C for 20 minutes with air agitation at the rate of 6.3 ml. per minute. The Underwood (30) and Thrust bearing corrosion tests provide examples of bearing corrosion tests in which the oil is oxidised during the test period. In the Underwood (30) oil at a temperature of 325°F is sprayed through air and impinges on a specimen of bearing metal. Catalysis in the test is provided by copper baffles in the machine. The sample size used is 1500 ml. and measurements are taken after 5, 10 and 15 hours. The Thrust bearing corrosion, or T.B.C. test (31) has a bearing surface subjected to a sliding action by steel at a pressure of 125 pounds per square inch for 20 hours. The oil temperature is 225°F.

Lacquer and sludge estimations are generally carried out in test engines. There are no standard laboratory tests but some workers have estimated lacquer by suspending a glass slide in oxidising oil and weighing the amount deposited (11). Sludge and insolubles are frequently measured by precipitating these from the oil by diluting with a suitable solvent, filtering and weighing the precipitate. The weight of insoluble recovered and its nature depend on the choice of solvent used.

Apart from corrosive wear there are no tests specially designed to test the mechanical properties of an oxidised oil. Tests for determining such factors as rate of wear, coefficient of friction, seizure load, etc., with lubricants in general can however be adapted for this purpose. By measuring the desired effect on the fresh oil and on the oxidised oil the effect of oxidation is ascertained.

Engine tests run in the laboratory under carefully controlled conditions are used in an attempt to approach true operating conditions when estimating the efficiency of a lubricant. Each test generally makes provision for the estimation of several factors. Lacquer is measured by dissembling the engine at the end of the test and inspecting the components. A points rating system is used to evaluate the lacquering, i.e. no lacquer rated at 10 to a heavy brown or black deposit rated at 0. Filters and oil lines are examined for sludge and insolubles.

Both corrosive and abrasive wear is measured in engine tests by weighing selected parts, usually piston rings, before and after operations.

More recently weighing has been replaced by having radioactive piston rings and estimating the wear from the radioactivity in the oil.

Most engine tests make provision for sampling the oil to allow various estimations to be made on it.

Engines operate under a wide diversity of running conditions of load, speed and temperature. Correspondingly a large number of engine tests have been devised. A number of these and their conditions have been standardised by the Co-ordinating Research Council of America (32). The L-1 test uses a single cylinder caterpillar diesel engine. Its main use is in the moderate oil temperature field. The L-3 uses a four cylinder caterpillar diesel engine. One of the most widely used engine tests of all is the L-4, operating in the high oil temperature range and using a regular Chevrolet engine. A G.M. diesel of three, four or six cylinders is used in the L-5 test.

Backoff describes an engine test used in the moderate temperature range using a Chovrolet engine (33). This, an often used test, is known as the FL-2.

A Lawson single cylinder engine has proved useful for oil testing due to its smallness, simplicity and low sample

requirement. Georgi has co-ordinated the test conditions of nineteen laboratories using this engine (34).

The table below gives the conditions for some of the familiar tests referred to and shows the diversity of standard conditions in use.

Test	Load h.p.	Speed r.p.m.	Oil Temp. °F	Duration Hours	Jacket Temp. °F
L - 3	37	1400	212	120	200
L - 4	30	3150	280	36	200
L - 5	27	2000	230	500	180
FL- 2	45	2500	155	40	95
Lauson	1.3 to 1.6	1600 to 1800	225 to 280	24 to 120	180-400

Advantages and Disadvantages of Laboratory and Engine Tests

Laboratory oxidation tests use simpler and cheaper apparatus. Their sample requirements are small. The number of variables in laboratory tests are low and kept to a minimum; there is thus a greater degree of control. However, it has been realised that results obtained in the laboratory are often not borne out in actual engine operation. An oil may be shown by conventional small scale tests to have good characteristics but be quite unsuitable in practice. This is more and more the case with compounded lubricants. The reason

for this is seen in the fact that laboratory tests tend to concentrate on one or a few aspects of oxidation or of the already oxidised oil. Although this enables a close study of the variable in question in actual practice the same variable may be obscured by other effects. Laboratory tests give good initial predictions.

Engine tests give a truer approach to the conditions under which the oil in question will be required to function. All the variables present in practice are present to some degree in the test engine. The results of such tests are more conclusive The disadvantages of engine tests lie in their cost and the degree of skill required in operating them and interpreting the results. Also the large number of variables present makes it difficult to decide which factor is causing what. Rather than being used on an analytical basis an engine is used more for proofing tests.

Purpose of Research

The purpose of the present investigation is to examine the changes taking place in oils of known analysis, during oxidation in the standard oxidation test of the Institute of Petroleum (38). The use to which the data is to be put is outlined below.

Any oxidation test must necessarily yield empirical results. Today there are, however, several fairly rapid and accurate methods for analysing oils. It is intended to show whether or not the more fundamental analysis figure is of more value in predicting the performance or liability to deteriorate, of an oil, than the result of an oxidation test. If the oxidation test result can be predicted from analysis then the test need not be performed. Part of this investigation, therefore, is to find how oils of different analysis behave in the oxidation test.

Necessary to the above is to find a suitable method of analysis. The best to date is the n - d - M but others have been proposed which are quicker and give essentially the same results. One of the purposes here is to examine a recent method, to test its accuracy against the n - d - M method and to try to speed up the process if possible.

The method of calculation in oil analysis is often laborious and it is intended to find how this can be speeded up. This would make the method suitable for routine operation.

Since the standard oxidation test referred to is widely used, an examination of the changes taking place during the time of oxidation is made. A number of physical constants and other factors are measured on oils of known analysis. This will provide data which can be compared with that obtained for oils oxidised in other designs of apparatus and under practical or operating conditions in engines. If it should be shown that the above changes are proportional to time of oxidation then it would be possible to shorten the time of the standard oxidation test. Where possible, attempts are made to explain changes in terms of oil analysis.

Much of the literature on oil oxidation contains details of oxygen absorption rate studies. These are usually made in apparatus of special design. It is proposed here to measure absorption (rate and quantity) taking place in the standard test.

The changes in the lubricating properties of oils which have undergone oxidation in the standard oxidation test are to be measured. This is to give data which enables the standard test to be compared with the practical aspect of lubricating oils.

ANALYSIS

The deterioration of lubricating oils by oxidation is dependent on the nature of the oils considered. With complex hydrocarbon mixtures this is not easy to define. The purpose of the following section is hence twofold:

i) To give as much information as is known about the history of the oil samples used before they reached the laboratory.

ii) To examine the most recent methods for analysing mineral oils and use them to examine the fractions worked on.

All oils used in the investigation were mineral oil fractions in the lubricant viscosity range. All had been refined to some extent but were free from any additives. Apart from two of the samples these were supplied by various oil companies.

The sample number, source of supply and any information given by the supplier regarding their origin and history is shown in Table I. Table II gives the constants, viz. refractive index, density, molecular weight and kinematic viscosity for each sample as measured by methods to be detailed later.

Seventeen samples have been used in this work. All of them have been incorporated to investigate two recent methods of structural group analysis to find their respective advantages. In the course of this work the analyses of the samples have been obtained.

The methods of analyses studied were the n-d-m method which

required measurements of refractive index, density and molecular weight and the V_K-n-d method using kinematic viscosity, refractive index and density. Some consideration was also given to the possibility of using the V_K-n-d method outwith the rather narrow limits specified for it.

TABLE I

Sample Number	Supplier	Source of Crude Oil and History
1	Sternol Ltd.	Mid Continent - Solvent refined neutral
2	do	Mid Continent - Solvent refined medium viscosity oil
3	do	Mid Continent - Solvent refined bright stock
4	"Shell" Research Ltd.	La Paz Oilfield, Venezuela - Prepared from a paraffinic type feedstock by furfural extraction, dewaxed and given a light earth treatment
5	Esso Development Company Limited	Kuwait - Prepared by distillation, phenol extraction, dewaxing and clay treatment
6	Supplied privately	Believed to be a mixture of crudes - no refining details
7	Supplied privately	Persian Gulf - no refining details
8	Esso Development Company Limited	Venezuela - Prepared by distillation, phenol extraction and clay treatment

TABLE I (Continued)

9	"Shell" Research Ltd.	Lagunillas Oilfield, Venezuela - Prepared from naphthenic type feed stock, vacuum distilled, treated caustic soda solution and vacuum distilled again
10	"Shell" Research Ltd.	Samples 10 to 17 inclusive represent a series of oils of increasing aromaticity supplied as requested.
11	do	
12	do	
13	do	
14	do	
15	do	
16	do	
17	do	

Sample Number	Ref. Ind. at 20°C n	Density at 20°C d	Molecular weight M	Kin. Viscosity at 20°C V_k
1	1.4807	0.8683	397	82.77
2	1.4889	0.8828	454	282.16
4	1.4858	0.8796	533	329.33
5	1.4803	0.8697	538	235.27
6	1.4854	0.8816	328	54.15
7	1.4898	0.8845	525	292.47
8	1.5016	0.9057	476	847.54
10	1.4736	0.8561	396	51.22
11	1.4804	0.8701	469	135.24
12	1.4830	0.8752	550	339.98
14	1.5052	0.9113	311	58.32
3	1.4920	0.8914	674	2076.6
9	1.5215	0.9453	410	1078.0
13	1.4920	0.8917	837	1947.0
15	1.5260	0.9463	366	523.61
16	1.5569	0.9841	264	77.07
17	1.5810	1.0193	339	5200.6

Table 2

The n-d-M method of Structural Group Analysis

Starting from the physical constants refractive index, n, density, d, and molecular weight, M, van Nes and van Westen describe a method for the Structural Group Analysis of mineral oil fractions based on the stastical analysis of a large number of samples (1). From general equations of the type:

$$C = \frac{a}{M} + b\Delta d + c\Delta n$$

$$R = a' + b'M\Delta d + C'M\Delta n$$

where C is the percentage carbon in one type of structure

R is the mean number of rings per molecule

Δd is the difference between measured density (d) and the density of the limiting normal paraffin (hypothetical paraffin containing infinite CH_2 groups, in the liquid state) at the same temperature.

Δn is the similar quantity for refractive index

M is the molecular weight

and a, b, c, a', b' and C' are constants

The percentage carbon in total ring structure (C_R), aromatic ring structure (C_A), the mean total number of rings per molecule (R_T) and number of aromatic rings per molecule (R_A) may be found.

Two equations are given for each quantity to be calculated, one for low range aromatics and one for high range. The reason for two sets of constants is not clear but is believed by the authors to be due to an assumption made when evolving the method not being strictly correct in the higher aromatic ranges. The assumption is that all aromatic rings are condensed each additional one after the first in the molecule contributing four carbon atoms.

The percentage carbon in paraffinic structure (C_p), naphthenic structure (C_n) and the mean number of naphthenic rings per molecule (R_n) are estimated by difference.

The method is intended for the Structural Group Analysis of olefin free petroleum distillates boiling above the gasoline range. It is considered suitable for, since it has been based on, samples which include fractions of molecular weight 194 and upwards, fractions containing 75 % carbon in ring structure where the aromatic rings do not exceed the naphthenic rings by more than 1½ times and fractions having up to four rings per molecule with not more than half of them aromatic.

Provided sulphur (S) does not exceed 2% a correction can be made for it.

The method is not suitable for individual hydrocarbons.

Determination

Refractive index (n) and density (d) are measured at 20°C and the molecular weight (M) is determined. If the sulphur content (S) is expected to exceed a few tenths of one per cent it is also estimated. These quantities are substituted in the following equations:

For measurements at 20°C

$$\Delta d = d - 0.8510$$

$$\Delta n = n - 1.4600$$

These in turn are used to determine two factors v and w used in subsequent calculations viz:

$$v = 2.51\Delta n - \Delta d$$

$$w = \Delta d - 1.11\Delta n$$

The percentage carbon in aromatic structure is given by:

$$\text{when } v \text{ is } +ve \quad C_A = 430v + \frac{3660}{M}$$

$$\text{when } v \text{ is } -ve \quad C_A = 6700 + \frac{3600}{M}$$

The percentage carbon in ring structure (naphthenic rings + aromatic rings) is given by:

$$\text{when } w \text{ is } +ve \quad C_R = 820w + \frac{10000}{M} - 3S$$

$$\text{when } w \text{ is } -ve \quad C_R = 1440w + \frac{10600}{M} - 3S$$

The percentage carbon in naphthenic structure and paraffinic structure is given respectively by

$$C_N = C_R - C_A$$

$$C_P = 100 - C_R$$

The mean number of aromatic rings per molecule is given by

when v is +ve $R_A = 0.44 + 0.055$ Mv

when v is -ve $R_A = 0.44 + 0.080$ Mv

The mean total number of rings per molecule (naphthenic + aromatic) is given by

when w is +ve $R_T = 1.33 + 0.146M\ (w - 0.005S)$

when w is -ve $R_T = 1.33 + 0.146M\ (w - 0.005S)$

The mean number of naphthenic rings per molecule is given by

$$R_N = R_T - R_A$$

A similar series of equations is available for measurements of refractive index and density at 70°C when these are not available at 20°C.

Van Nes and van Westen in their original publication (1) give a series of nomographs for solving the equations mechanically

The V_k-n-d method of Structural Group Analysis

Boelhouwer and Waterman give a method for the Structural Group Analysis of mineral oils based on kinematic viscosity (V_k), refractive index (n) and density (d) (3).

In a preliminary publication Boelhouwer, van Steenis and Waterman indicate a graphical relationship between kinematic viscosity of saturated or hydrogenated mineral oils and their structure (35). Taking as the axes of a graph the logarithm of kinematic viscosity ($\log V_k$) and refractive index, lines of constant density and ring content (mean number of rings per molecule) (R_T) are drawn. The way in which the relationship may be used to determine the mean number of rings per molecule in a hydrogenated oil fraction is indicated. Boelhouwer and Waterman in the publication referred to initially, extend the graph to include curves of constant molecular weight (M) and percentage carbon in ring structure (C_R). Figure 1 shows the graph.

The method is further developed to include oil fractions containing aromatic rings. By means of equations involving a factor Δd,* the physical constants (kinematic viscosity and density) that the aromatic fraction would have if it were completely hydrogenated may be predicted and the point

*The difference between the density of a hydrogenated oil having the same kinematic viscosity and refractive index as the sample to be analysed (from Fig. 1) and the density of the sample itself

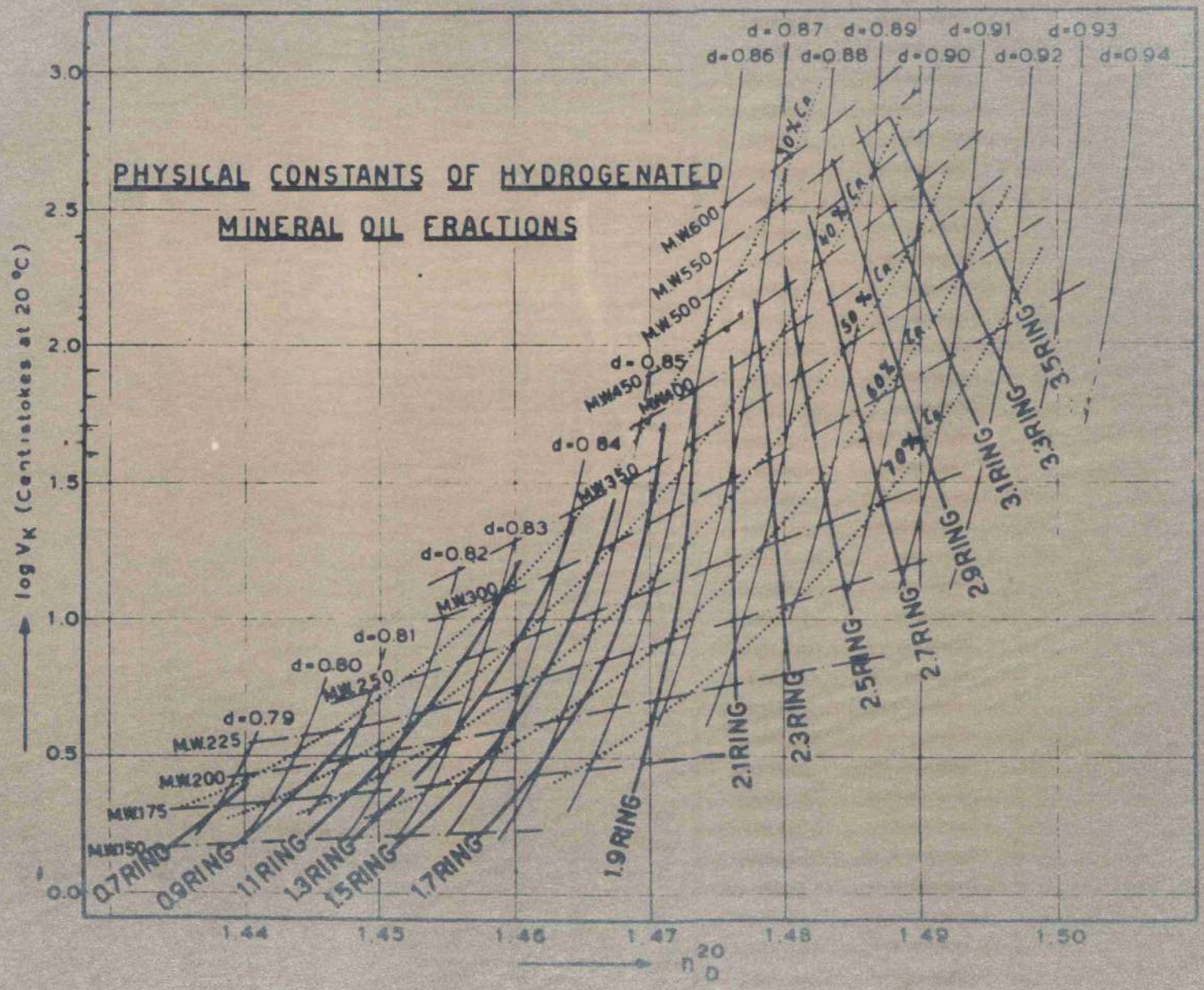

PHYSICAL CONSTANTS OF HYDROGENATED
MINERAL OIL FRACTIONS
log V_K (Centistokes at 20 °C)
n_D^{20}
d=0.86
d=0.87
d=0.88
d=0.89
d=0.90
d=0.91
d=0.92
d=0.93
d=0.94
d=0.85
d=0.84
d=0.83
d=0.82
d=0.81
d=0.80
d=0.79
M.W600
M.W550
M.W500
M.W450
M.W400
M.W350
M.W300
M.W250
M.W225
M.W200
M.W175
M.W150
10% Ca
20% Ca
30% Ca
40% Ca
50% Ca
60% Ca
70% Ca
0.7RING
0.9RING
1.1RING
1.3RING
1.5RING
1.7RING
1.9RING
2.1RING
2.3RING
2.5RING
2.7RING
2.9RING
3.1RING
3.3RING
3.5RING
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.44
1.45
1.46
1.47
1.48
1.49
1.50

Fig 1

corresponding to these obtained on the original graph. As molecular weight, percentage carbon in ring structure and the total number of rings per molecule are the same for the aromatic oil and the same oil when hydrogenated these values can be read from the graph.

The percentage carbon in aromatic structure (C_A) is given by an equation in ΔD. Two equations one for low range values, one for high, give the mean number of aromatic rings per molecule (R_A). Percentages of carbon in paraffinic structure (C_p), naphthenic structure (C_N) and the mean number of naphthenic rings per molecule (R_N) are obtained by difference.

Provided the percentage sulphur (S) in a fraction is reasonably low it may be corrected for.

Natural limits are placed on the method by the boundaries of the graph - Figure 1 - used.

Determination

Measurments of kinematic viscosity (V_k) in centistokes, refractive index (n) and density (d) are made at 20°C. The percentage sulphur (S), if it is appreciable, is estimated.

Taking the logarithm of kinematic viscosity ($\log V_k$) and the refractive index a density d' is read from Figure 1.

This is used to obtain factor Δd viz:

$$\Delta d = d' - d$$

The density d^* of the theoretically completely hydrogenated oil is ascertained from:

$$d^* = d - 0.62\Delta d - 0.008S$$

The logarithm of kinematic viscosity $\log V_k^*$ of the theoretically completely hydrogenated oil is given by:

$$\log V_k^* = (1 - 3\Delta d) \log V_k + \Delta d$$

Using d^* and $\log V_k^*$ in Fig. 1 the molecular weight (M), percentage carbon atoms in total ring structure (C_R) and the mean total number of rings per molecule (R_T) are read.

The percentage carbon atoms in aromatic structure is estimated from Δd viz:

$$C_A = 600\Delta d - (40\Delta d)^2$$

and the average number of aromatic rings per molecule from:

$$2R_A + 1 = \frac{M \times C_A}{2,800} \quad \text{where } R_A > 1$$

$$3R_A = \frac{M \times C_A}{2,800} \quad \text{when } R_A < 1$$

The percentage carbon in naphthenic structure and paraffinic structure is given respectively by $C_N = C_R - C_A$ and

$$C_p = 100 - C_R$$

The mean number of naphthenic rings per molecule is given by

$$R_N = R_T - R_A$$

Nomographs

By their nature the equations required by the V_k-n-d method ar laborious to solve. Van Nes and van Westen overcame similar difficulty by the construction of four nomographs to resolve, quickly and less laboriously, the equations required by the n-d-M method. The value of these led to the construction of nomographs for the mechanical solution of the V_k-n-d equations. By suitable scale layout a solution could be achieved using three nomographs. The complete analytical technique reduces to the determination of the three physical constants and the use of four diagrams (the graph plus three nomographs).

The nomographs, shown in Figs. 2, 3 and 4, require ten scales. These are numbered for easy description. Fig. 2 containing scales I to IV gives Δd, d^* and C_A already defined. By taking a straight line between d and d' and extending it to cut the other scales Δd and C_A are given on scale III and d^* on scale IV. Due to the closeness of scales I and II it is found to be of some advantage if the third decimal place of Δd is obtained by inspection and the line accurately placed at this before reading d^*.

Scales V and VI on Fig. 3 give $V_k - \Delta d$ on scale VII. The simple addition of Δd to this gives V_k^*. Fig. 4 gives R_A - no selection of the two possible equations being necessary this being accounted for by the scales.

The nomographs do not take into account the sulphur correction to d^* which is not often required. When this is necessary it is done as explained in the original method, i.e. subtraction of 0.008S from d^*.

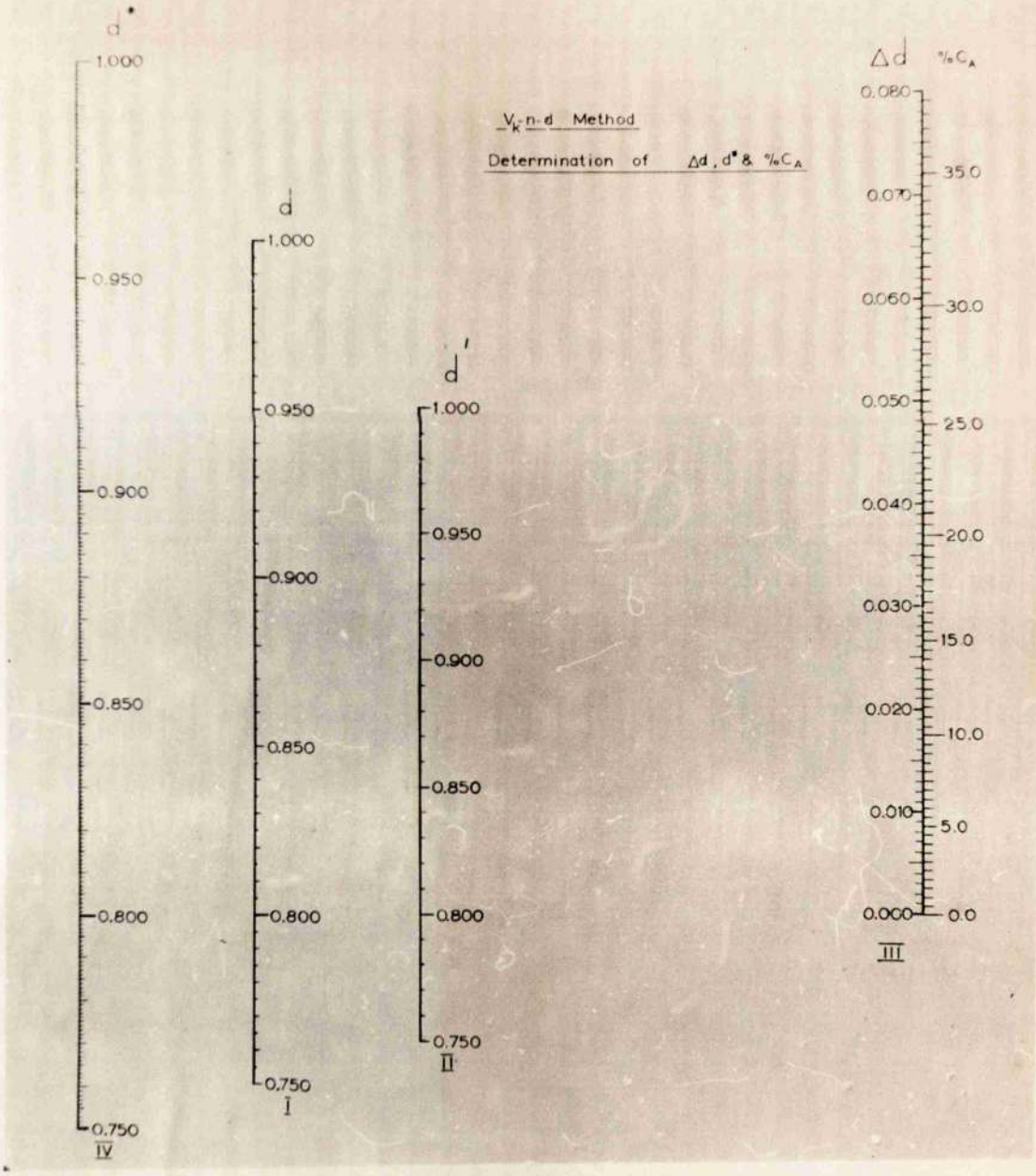

V_K n-d Method
Determination of Δd, d* & %C_A
d*
1.000
0.950
0.900
0.850
0.800
0.750
IV
d
1.000
0.950
0.900
0.850
0.800
0.750
I
d'
1.000
0.950
0.900
0.850
0.800
0.750
II
Δd
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
%C_A
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
III

Fig 2

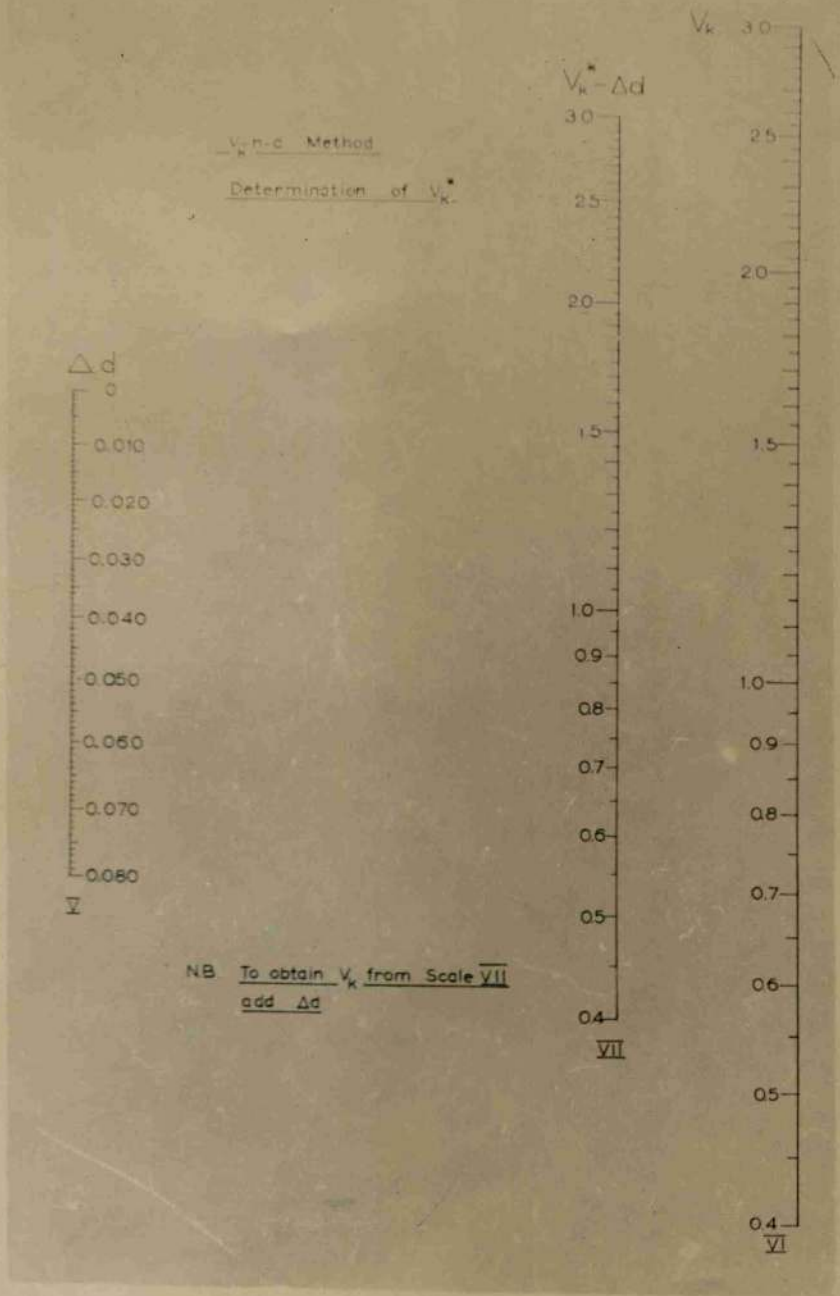

V_k n-d Method
Determination of V_k^*
Δd
0
0.010
0.020
0.030
0.040
0.050
0.060
0.070
0.080
V
$V_k^* - \Delta d$
3.0
2.5
2.0
1.5
1.0
0.9
0.8
0.7
0.6
0.5
0.4
VII
V_k
3.0
2.5
2.0
1.5
1.0
0.9
0.8
0.7
0.6
0.5
0.4
VI
N.B. To obtain V_k from Scale VII add Δd

Fig 3

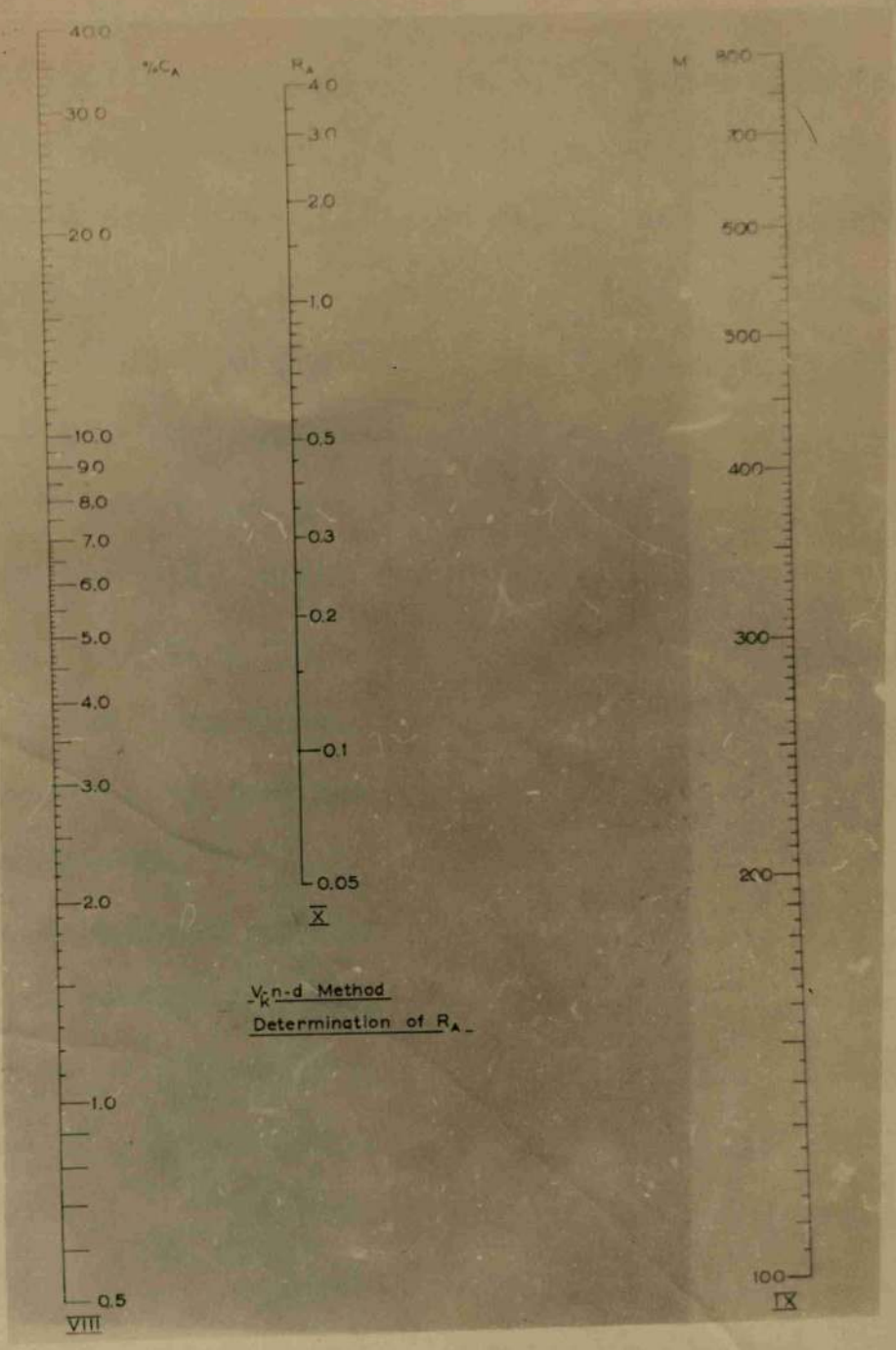

40.0
30.0
20.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.5
%C_A
VIII
R_A
4.0
3.0
2.0
1.0
0.5
0.3
0.2
0.1
0.05
X
M
800
700
600
500
400
300
200
100
IX
V_K n-d Method
Determination of R_A

Fig 4

Experimental Procedure

The refractive indices, densities, molecular weights and kinematic viscosities were measured on seventeen oil samples by the methods explained later. The values obtained are already shown in Table 2. These were substituted in the appropriate method and the n-d-M and V_k-n-d analyses obtained for each sample. On substitution, six of the oil samples were found to be outwith the graph used in the V_k-n-d method. The constants of the oils which could only be analysed by the n-d-M method (assuming no extrapolation of the V_k-n-d graph) are shown in the second section of Table 1. The first section contains the bulk of the samples and these could be analysed by both techniques.

All calculations of the V_k-n-d analysis were carried out using the nomographs constructed and a specimen calculation is presented. Table 3 gives a suitable layout for quick estimation. The first column contains the measured constants of the fraction and intermediate quantities in the calculation, the other two give carbon distribution and ring content respectively. For comparison sample calculations for the same fraction analysed by the n-d-M method are given in Table 4 using the nomographs supplied by the authors.

Complete analysis figures for the oils which could be analysed by both methods were evaluated and the comparisons are given in Tables 5 and 6 .

To obtain an accurate evaluation the results were examined by the "t" test of statistics. A short explanation of the test is given at the end of this section and the results of the test shown in Table 7.

For the six oils outwith the V_k-n-d graph, a process of extrapolation of the graph (Fig. 1) was tried to find the reliability of this operation. Table 8 shows the results obtained and the corresponding results given by the n-d-M analysis of the samples. The differences between the two sets of results are also in the Table.

Constants		Carbon Distribution		Ring Content and Mol. Wt.	
log V_k	2.3716	C_A	3.1	R_T	2.30
n	1.4803	C_R	30.0	R_A	0.19
d	0.8697	C_p	70.0	R_N	2.11
d'	0.8750	C_N	26.9	M	520
Δd	0.0053				
d^*	0.8665				
Log V_k^* - Δd	2.330				
Log V_k^*	2.335				

Table 3

Constants		Carbon Distribution		Ring Content	
n	1.4803	C_A	3.3	R_A	0.21
d	0.8697	C_R	29.0	R_T	2.35
M	538	C_N	25.7	R_N	2.14
v	-0.50	C_p	71.0		
w	-0.45				

Table 4

NOTE: All measurements at 20° C.

Sample Number	n - d - M					V_k - n - d				
	Mol. Wt.	C_p	C_n	C_A	C_R	Mol. Wt.	C_p	C_n	C_A	C_R
1	397	57.3	36.2	6.5	42.7	400	65.5	27.7	6.8	34.5
2	454	64.2	26.3	9.5	35.8	490	65.5	26.0	8.5	34.5
4	533	67.5	26.3	6.2	32.5	525	67.0	28.3	4.7	33.0
5	538	71.0	25.7	3.3	29.0	520	70.0	26.9	3.1	30.0
6	328	54.5	36.9	8.7	45.6	325	51.0	42.5	6.5	49.0
7	525	67.0	24.1	8.9	33.0	480	63.5	27.9	8.6	36.5
8	476	58.3	28.7	13.0	41.7	535	60.0	28.5	11.5	40.0
10	396	69.3	27.0	3.7	30.7	385	67.5	29.6	2.9	32.5
11	469	67.7	28.1	4.2	32.3	450	65.5	31.0	3.5	34.5
12	550	69.0	26.8	4.2	31.0	545	68.0	28.9	3.1	32.0
14	311	46.0	35.4	18.6	54.0	285	42.0	38.1	19.9	58.0

Table 5

Sample Number	n - d - M			V_K - n - d		
	R_N	R_A	R_T	R_N	R_A	R_T
1	1.68	0.32	2.00	1.59	0.32	1.91
2	1.88	0.55	2.43	2.02	0.50	2.52
4	2.30	0.34	2.64	2.30	0.30	2.60
5	2.14	0.21	2.35	2.11	0.19	2.30
6	1.95	0.31	2.26	2.10	0.25	2.35
7	2.11	0.56	2.67	2.13	0.50	2.63
8	2.33	0.77	3.10	2.60	0.73	3.33
10	1.54	0.16	1.70	1.56	0.14	1.70
11	2.02	0.22	2.24	2.01	0.19	2.20
12	2.30	0.25	2.55	2.40	0.20	2.60
14	1.86	0.70	2.56	1.88	0.67	2.55

Table No. 6

ITEM	MEAN DIFFERENCE	STANDARD DEVIATION	STANDARD ERROR OF MEAN	t	PROBABILITY FOR n = 10
M	+ 4.0	+ 29.0 −	9.0	0.40	0.7 - 0.6
C_P	+ 1.0	+ 3.7 −	1.0	1.04	0.4 - 0.3
C_R	- 1.0	+ 3.7 −	1.0	1.04	0.4 - 0.3
C_N	1.3	+ 3.8 −	1.1	1.11	0.3 - 0.2
C_A	+ 0.7	+ 1.0 −	0.3	2.42	0.05 - 0.02
R_T	- 0.02	+ 0.09 −	0.03	0.63	0.6 - 0.5
R_N	- 0.05	+ 0.12 −	0.04	1.62	0.2 - 0.1
R_A	0.04	+ 0.02 −	0.06	0.65	0.6 - 0.5

Table No. 7

Table No. 8

SAMPLE	N-d-M ANALYSIS							EXTRAPOLATION of V_K-n-d GRAPH						
No.	M	C_A	C_N	C_P	R_A	R_N	R_T	M	C_A	C_N	C_R	R_A	R_N	R_T
3	674	6·8	25·7	32·5	0·56	2·94	3·5	660	5·5	25·5	31·0	0·43	2·97	3·40
9	410	25·2	28·8	54·0	1·30	2·19	3·49	400	25·0	33·0	58·0	1·30	2·35	3·65
13	837	5·5	24·5	30·0	0·57	3·46	4·03	730	6·1	25·9	32·0	0·53	2·87	3·40
15	366	24·1	34·6	58·7	1·10	2·28	3·38	350	24·0	39·0	63·0	0·98	2·52	3·5
16	264	45·2	26·8	72·0	1·50	1·50	3·0	245	34·9	47·1	82·0	1·60	2·30	3·3
17	339	52·8	18·2	71·0	2·31	1·53	3·84	350	39·0	45·0	84·0	1·90	2·70	4·60

Differences between results obtained by the two methods:
(n - d - M result) - (V_K - n - d result)

SAMPLE No.	M	C_A	C_N	C_R	R_A	R_N	R_T
3	+ 14	+ 1·3	+ 0·2	+ 1·5	+ 0·13	- 0·03	- 0·10
9	+ 10	+ 0·2	+ 4·2	- 4·0	0	- 0·16	- 0·16
13	+ 100	- 0·6	- 1·4	- 2·0	+ 0·04	+ 0·60	- 0·06
15	+ 16	+ 0·1	- 4·4	- 4·3	+ 0·12	- 0·24	- 0·12
16	+ 9	+ 10·3	+ 20·3	- 10·0	+ 0·50	- 0·80	- 0·30
17	- 11	+ 13·8	- 26·8	- 13·0	+ 0·41	- 1·17	- 0·76

The Measurement of Refractive Indices

Refractive Indices were measured by an Abbe Refractometer, regularly checked with distilled water. All measurements were made at 20°C using the Sodium - D - line.

The Measurement of Density

A simple technique using a U-tube pycnometer was evolved to measure densities.

The pycnometer employed was a modification of the Cup-type pycnometer recommended by van Nes and van Westen, for use in the n-d-M method (1) and described by Lipkin, Mills, Martin and Harvey (36). The essential difference here was the omission of ground glass removeable cups on each limb. These had been intended to provide traps for expansion should the temperature of weighing exceed that of measurement and reservoirs when the filling temperature exceeded the measurement temperature. As measurements in the foregoing work were generally made at temperatures of the same order or higher than those of weighing and filling, the quantities involved were small and thus in the case of such viscous non volatile liquids could be contained as droplets on the tops of the limbs. The method recommended by Lipkin et al (36) for buoyancy correction during weighing was used, i.e. no correction was applied to weighings during the calibration or density

measurement but an apparent volume was found which was used to obtain the apparent density. This differed from the actual density by a maximum of three units in the fourth decimal place. When accuracy at this level was required a final correction could be applied by means of an equation to give the true density in vacuo.

Design

The pycnometer, Figure 5a, consists of a U-shaped tube of 1 mm capillary with a bulb blown in one limb. The top of each limb is ground flat and glass lugs are fitted which allow a suspension hook to be attached. Volumes are from 6 to 8 ml.

Filling, Emptying and Cleaning

These operations are carried out by means of a filter pump with a trap fitted as shown in Figure 5b. Rubber connections, which deteriorate under the action of hydrocarbons, are kept to a minimum and frequently replaced. Figure 5b shows the arrangement for filling. The limb containing the bulb is immersed in the liquid to be measured and the connection from the trap is attached to the other limb. With oils of low viscosity gentle suction is used, with more viscous material the pycnometer is left to fill under full available suction. When completely filled the pump is disconnected, before removal of the instrument from the oil.

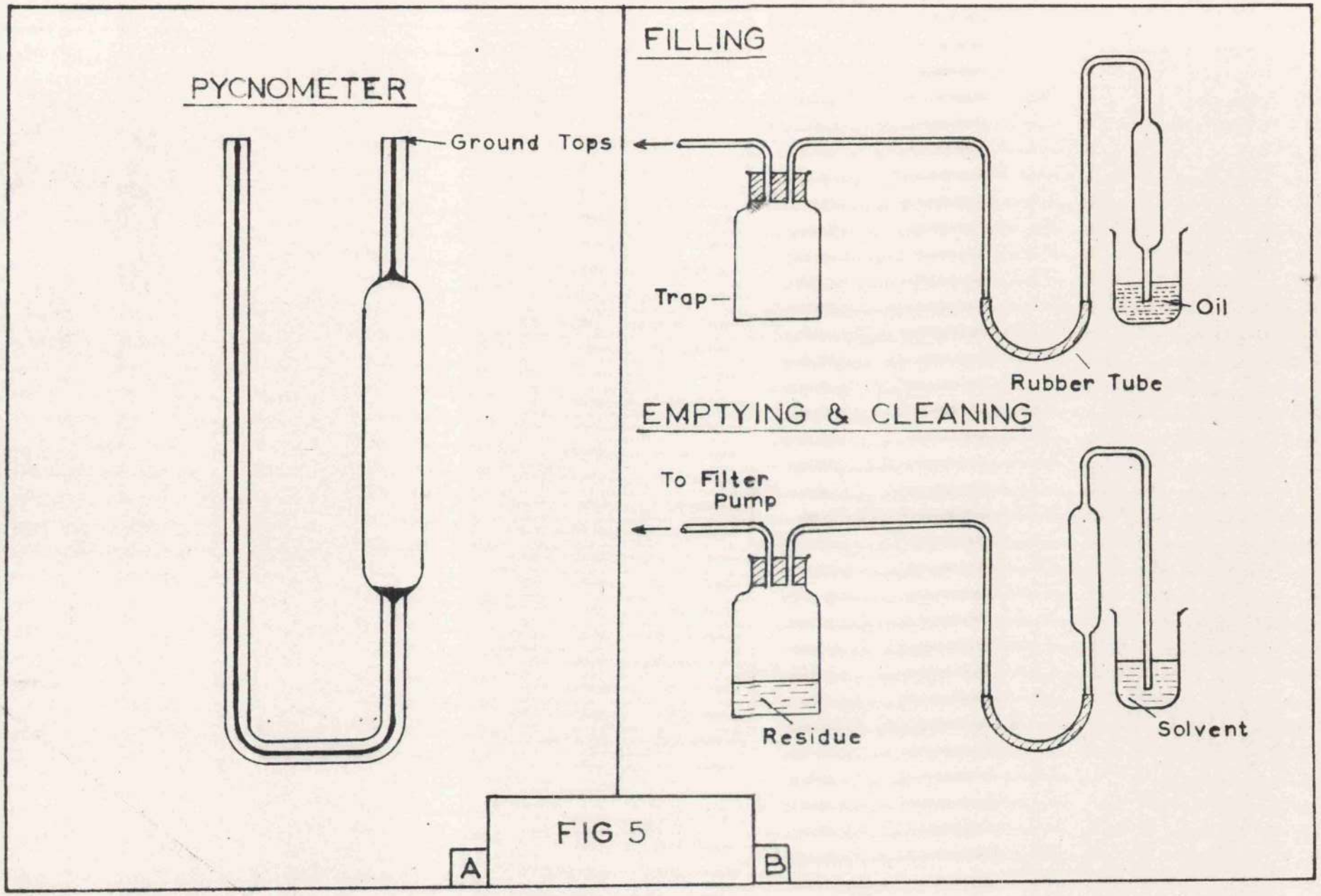

PYCNOMETER
Ground Tops
FILLING
Trap
Oil
Rubber Tube
EMPTYING & CLEANING
To Filter Pump
Residue
Solvent
A
B

FIG 5

Excess oil is wiped from the top of each limb before immersion in the thermostat.

When the pycnometer is to be emptied, the suction tube is connected to the limb containing the bulb and the oil sucked into the trap. A beaker of solvent, petroleum ether or benzene (acetone in the case of aqueous material) is then placed as shown in Figure 5b and the solvent allowed to sweep through to remove the oil. When no oil remains the beaker is removed and sucking continued to air dry the instrument.

Calibration

The apparent volume of the pycnometer was found using freshly distilled water as follows.

The clean dry pycnometer was washed on the outside with acetone to remove any static charge, suspended by its hook on the balance and weighed to the nearest 0.1 mg.. It was filled as described and suspended in a thermostat maintained at 20°C ± 0.05°C for twenty minutes. Excess water was then removed from the tops of the limbs with absorbent paper. The pycnometer was removed, cleaned and dried on the outside and washed down with acetone before weighing. The apparent volume was found by dividing the weight ofwater in air by the density of water at 20°C (0.99823 gm./ml.)

Determination

The technique used to determine oil densities was the same as that described for calibration except that the ground glass tops were wiped with a clean cotton cloth instead of absorbent paper. The apparent density was calculated by dividing the weight of oil in air by the apparent volume of the pycnometer. By adding a correction factor (C) to the apparent density (d_A), the true density in vacuo was obtained.

The equation for the correction factor is, according to Lipkin (36), $C = 0.0012 (1 - d_A)$.

The Measurement of Molecular Weight

Two methods are available for determining the molecular weights of high boiling oil fractions. Both entail adding an increment of the oil to a suitable solvent. The cyroscopic method depends on the resultant depression of the freezing point, the ebullioscopic on the elevation of the boiling point. Apparatus requirements are simpler for the former method but indications are that the results obtained may differ considerably from the true values. Mair quotes a number of references to this effect (37).

The ebullioscopic method is recommended by van Nes and van Westen (1) for the n-d-M analysis and it has been used in the foregoing work.

When a quantity of oil is added to a suitable solvent it can be shown that, under ideal conditions, the resulting rise in boiling point is related to the molecular weight of the oil by the equation

$$M = K \frac{c}{\Delta T} 100$$

where M = Molecular weight of oil

C = Concentration of oil in solvent (gms per gm)

ΔT = Elevation of boiling point

K = Ebullioscopic constant

In practice ideal conditions are not realised and the molecular weight as calculated from the formula is not the same at all concentrations. Mair (37) and van Nes and van Westen (1) recommend that the molecular weight indicated by zero concentration be taken. This is found by plotting molecular weight or boiling point elevation at a number of concentrations and extending the best line among the points to meet the molecular weight axis.

Measurements are made in an ebullioscope, a vessel fitted with a condenser and containing boiling solvent. Provision is made for heating, temperature measurement and oil addition. A number of factors have to be taken into account in the design and operation ofebullioscopes. The boiling point of the solvent changes as the atmospheric pressure varies during

a test to give false temperature differences. By operating two ebullioscopes side by side, one of which contains only boiling solvent, any change in the boiling point may be noted and a corresponding correction made to the indicated temperature difference.

Superheating is eliminated by having a Cottrell vapour lift pump which ensures a steady stream of liquid in intimate contact with vapour flowing over the thermometer bulb.

A certain amount of solvent is always out of solution in the form of vapour and hold up in the condenser. This gives a calculated concentration, based on the weight of solvent, less than the actual. By ensuring a controlled boiling rate to give a constant hold up this factor is accounted for by the ebullioscopic constant of the instrument.

Description of Apparatus

The ebullioscope, a modified version of that described by Mair (37), is shown in Figure 6. Designed for easy replacement, it uses a standard condenser and standard ground glass joints. Temperatures are measured on a Beckman thermometer held in the upper part by a cork. The underside of the cork is coated with "Araldite", a resin material which sets hard and is unaffected by boiling solvent. This prevents saturation of the cork and solvent leakage. The two legs of the Cottrell pump are directed on to the thermometer bulb and both pump and bulb are protected from cooled solvent, returned from

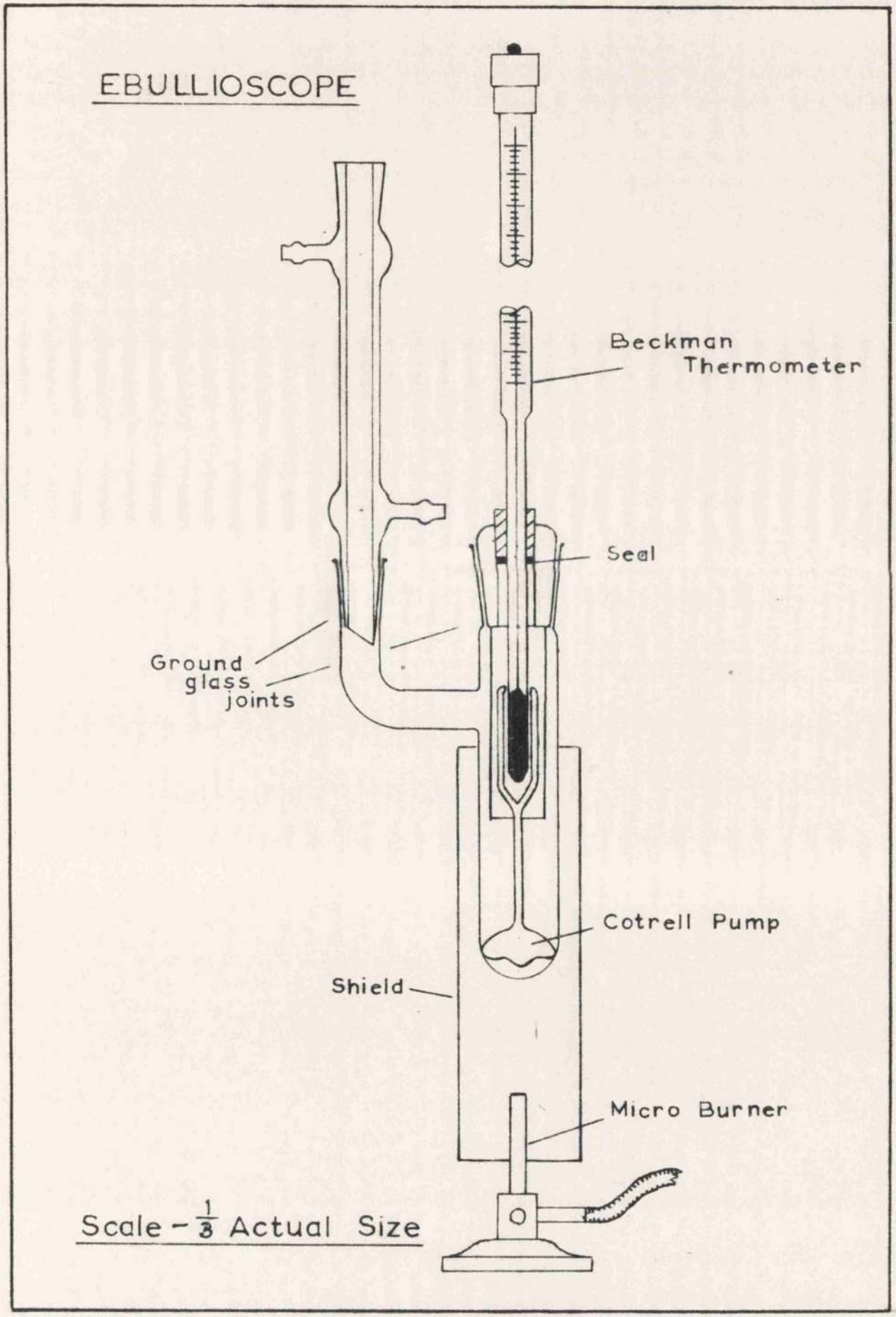

EBULLIOSCOPE
Beckman
Thermometer
Seal
Ground
glass
joints
Cotrell Pump
Shield
Micro Burner
Scale - 1/3 Actual Size

FIG 6

the condenser, by a length of glass tube. Heating is by a micro gas burner controlled by a screwclip on the burner tubing. A six inch length of two inch diameter glass tube shields burner and solvent-containing section of the ebullioscope. The apparatus operates on forty mls. of solvent.

Two ebullioscopes are operated side by side in a glass case, because of the adverse effects of draughts on the thermal equilibrium of the system.

Oil additions are made by means of a short length of burette (total length approximately six inches) with a suspension hook for weighing. The burette, containing oil, is clamped above the vertical condenser and oil allowed to drop to the foot where it is washed into the solvent. Accurate control of increment size by the stopcock (lubricated by the oil being added) enables any desired temperature elevation to be realised.

Determination

Benzene was found to be a suitable solvent and was used exclusively.

Before a determination both ebullioscopes were boiled with 40 mls. of pure benzene followed by emptying, drying and refilling of the one to be used for measurements with exactly 40 mls. of benzene measured at 20°C. Boiling was recommenced and the rate adjusted to give a suitable hold up (two drops per second returned from the condenser). When the temperature recorded by the Beckman thermometer was constant to within

0.005°C the first addition was made to give an initial elevation of 0.2 to 0.3°C. Reweighing the burette gave the weight of oil added by difference. Further successive increases in the boiling point elevation of approximately 0.1°C were obtained by adding increments of oil until a total temperature rise of 1°C was recorded. The exact temperature at the start and after each addition was recorded to the nearest .001°C, weighings were to the nearest milligram.

Experience showed that the shorter the time lapse between the start and finish of a test the more reproducible the results. For this reason only one reading of temperature was taken after an addition (sufficient time being allowed for the apparatus to stabilise) instead of the mean of several. Any slight deviations from the mean were averaged out over all the additions. Simultaneously with these readings the temperature of the pure boiling solvent was recorded.

A number of barometer readings were made throughout a determination in order to correct the ebullioscopic constant for pressure changes.

Calculation

It was desirable to obtain the molecular weight corresponding to the concentration after each oil addition and before the next was made. This involved solving equation I quickly.

Taking the ebullioscopic constant as 27 (an average value found for benzene) and the weight of 40 mls. of pure benzene at 20°C as 33.1760 gms. the equation reduces to

$$M = 0.768 \frac{\Delta T}{w}$$

where w = weight of oil increment

Figure 7 shows the nomograph for solving this. By taking a straight line between ΔT (appropriately corrected for any change in solvent boiling point) and w on the axes indicated the intersect on the centre axis gives the molecular weight. The values so obtained are plotted against boiling point elevations and the best line among points extended to zero boiling point elevation to give the molecular weight assuming an ebullioscopic constant of 27. The value so obtained has to be adjusted for any difference between the actual constant and 27, which there invariably will be since it is a function of the instrument and atmospheric pressure. The correction to be added is given by

$$(K' - 27)M$$

Where K' = ebullioscopic constant at time of determination.

The ebullioscopic constant is obtained for the instrument by calibration with compounds of known molecular weight in a manner similar to the determination of molecular weight.

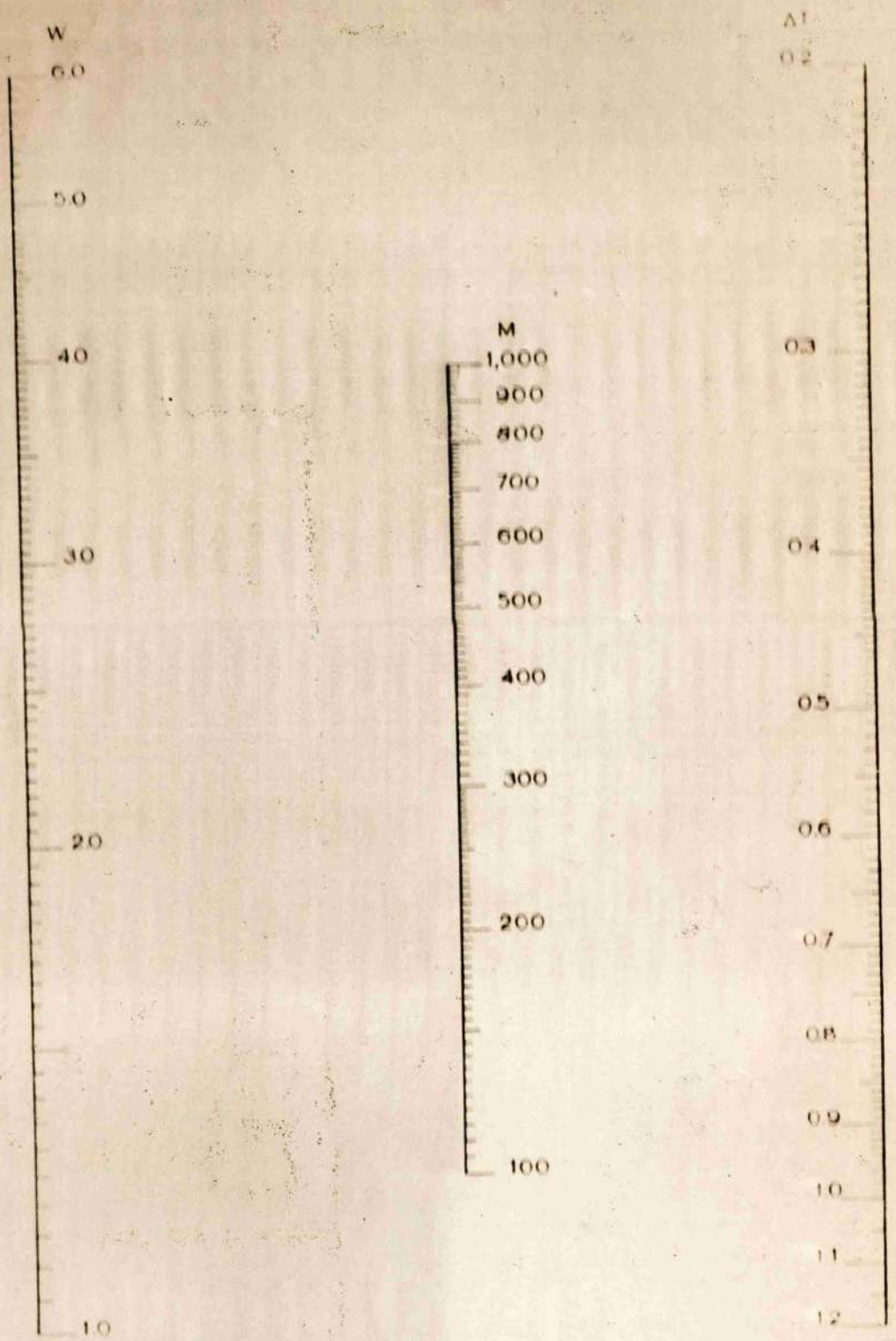

W
60
50
40
30
20
10
M
1,000
900
800
700
600
500
400
300
200
100
Δ1
02
03
04
05
06
07
08
09
10
11
12

Fig 7

Tetralin (M.Wt. = 132) and naphthalene (128) were used, the later being added in pellet form. Equation I was used to determine K and the values obtained plotted to a base of boiling point elevation (ΔT). The best straight line among points was extended to cut the axis at zero ΔT and this value taken as the ebullioscopic constant (K_a) for the instrument at the mean atmospheric pressure (p_o) at which the calibration was made.

Van Nes and van Westen (1) give an equation to correct the ebullioscopic constant for pressure changes. It is

$$K' = K_o + 0.24 (p_o - p)$$

where p = atmospheric pressure during determination

The Measurement of Kinematic Viscosity

Kinematic viscosities were measured by U-tube viscometers kept at 20°C in thermostated baths. The method was according to the Institute of Petroleum "Viscosity (Kinematic) Absolute Units" IP - 71/47 Method C. Calibration of viscometers was according to British Standard Specification B.S. 188.

The t-Test

The t-test of statistics evolved by "Student", gives a suitable method of determining whether the results given by two different methods, designed to yield the same answer, are significantly different or not.

If a number of samples are analysed by the two methods and it is desired to show that they do not differ the null hypothesis is adopted and it is assumed that there is a difference in the methods. The difference between individual results is then taken (i.e. Result obtained by first method - Result obtained by second). These may be represented by x_1, x_2, x_3 etc. and they will have a mean value $\bar{x}$. If there are n results in all there will be (n-1) degrees of freedom and the standard deviation will be given by S

$$\text{where } S = \frac{\Sigma(x-\bar{x})^2}{n-1}$$

and the standard error of the mean will be given by

$$\frac{S}{\sqrt{n}}$$

The quantity t is given by the ratio of the mean of the differences ($\bar{x}$) to the standard error of the mean and tables of t give the probabilities of t for any given number of degrees of freedom.

Each of the above statical quantities has been estimated for each of the items given by the n-d-M and V_k-n-d methods of analysis and shown in Table 7.

It is generally accepted that if the probability is 0.05 or greater then there is no significant difference, if it lies between 0.05 and 0.01 then the difference is in the statical sense probably significant and results less than 0.01 show that the difference is significant.

As seen in Table 7 all results except that for C_A show that there is no significant difference and the null hypothesis can be rejected. In the case of C_A the difference between methods is probably significant and it remains to examine the results obtained and determine to what extent the results are affected.

Discussion of Results

The purpose of the V_k-n-d method of Structural Group Analysis is to dispense with the difficult and unstandardised measurement of molecular weight and replace it by the standard measurement of kinematic viscosity. As a result the time saved in obtaining the constants is considerable (molecular weight may take more than an hour) and the degree of precision and technique required is much less.

When the constants are obtained the time and effort required to calculate the analysis figures is the same in either case but the V_k-n-d method entails the use of a graph with its attendant estimations of interpolated points which may lead to inaccuracies as against a complete solution by equations in the n-d-M method. It must also be remembered that the V_k-n-d method is derived from a lesser amount of fundamental data in the form of samples of known analysis and consequently the n-d-M must be regarded as the more accurate technique.

As explained earlier and as seen from the results obtained the limits of the V_k-n-d method are much narrower and consequently the method is found to be of less general applicability. The aforesaid limits are particularly inconvenient in the high aromatic ranges.

The analysis of the eleven samples which were within the range of the V_k-n-d method have been compared with the corresponding n-d-M analysis in Tables 5 and 6. Visual inspection shows favourable comparison and when the results are examined statistically, in Table 7 by the t-test it is shown that for all quantities except C_A the differences in the methods are not significant. Results for C_A show that the difference between the methods is probably significant, in the statistical sense, but when the results are considered it is seen that although the n-d-M method tends to give higher results than the V_k-n-d, the mean difference for the eleven results is only 0.7% in C_A, i.e. the n-d-M on the average can be expected to give a value for C_A 0.7% higher than the V_k-n-d.

Table 8 shows the results of analysis by the n-d-M method and the V_k-n-d method when extrapolation of the graph had to be employed. Also shown are the differences obtained in the results of both methods. In general when extrapolation is along the log V_k axis of Figure 1, the results obtained are comparable. This is because the lines of constant density are almost parallel to the log V_k axis in this region and extrapolations can be easily and accurately made; viz. samples 3, 9 and 13. With high aromatic samples, however, which have high refractive indices, results do not compare favourably as seem with samples 16 and 17. The process of extrapolation is more difficult especially the fundamental estimation of

density from the graph. However the difficulty of extrapolation does not alone account for the large differences here in the two methods. It was assumed that for some reason the V_k-n-d relations break down in the high aromatic region and an examination was made of the equation provided for estimating C_A which is

$$C_A = 600\ d - (40\Delta d)^2$$

It can be shown that by differentiating C_A with respect to Δd that there is a maximum possible value that C_A can have.

$$\text{i.e.} \frac{dC_A}{d\Delta d} = 600 - 3200\ d$$

and when $\frac{dC_A}{d\Delta d} = 0$ $\quad \Delta d = 0.188$

and when Δd has this value $C_A = 57\%$

Hence the equation has a limiting value of carbon in aromatic structure of 57% and the nearer the percentage of carbon atoms in aromatic structure approach this the less accurate the estimation of C_A is likely to be.

The conditions of use of the V_k-n-d method instead of the n-d-M can be summarised, therefore, as follows:

i) It can be used with confidence when the constants measured lie within the graph supplied.

ii) It is safe to extrapolate along the log V_k axis.

iii) Extrapolation along the refractive index axis is an indication of high aromatic content and will certainly yield erroneous results.

The Standard Oxidation Test.

The following section considers the behaviour of refined lubricating oil fractions of known analysis in the "Standard Oxidation Test for Lubricating Oils" of the Institute of Petroleum I.P 4/44 (38).

Structural Group Analyses of the oils have been obtained in the previous section.

In the first instance the relationship between analyses and the results obtained in the standard test, performed according to specification, has been investigated.

During the analysis of results it was seen that some factor undefined the analysis and physical constants of the oil was active. This was believed to be due to the fact that oils of similar structural group analysis may have different molecular analysis. An attempt has been made to minimise this effect by studying a series of samples from the same original oil which had been subjected to progressive extraction to remove aromatics.

A study of the rate and quantity of oxygen absorbed from the oxidising air during the standard test has been made.

Concluding the section is an investigation of the way in which some physical constants of oils vary with time of oxidation in the standard test apparatus.

Experimental Procedure

The standard oxidation test, outlined below, has been carried out on the seventeen petroleum fractions analysed in the previous section. Table 9 gives the results and shows the main items in the structural group analysis, the kinematic viscosity at 100°F, the viscosity ratio and the increase in carbon residue. The carbon residue results have further been plotted against the percentage carbon in aromatic structure in Figure 10. An attempt to plot a similar curve for viscosity ratio showed no simple relationship.

The Standard Oxidation Test of the Institute of Petroleum I.P. - 48/44 (38)

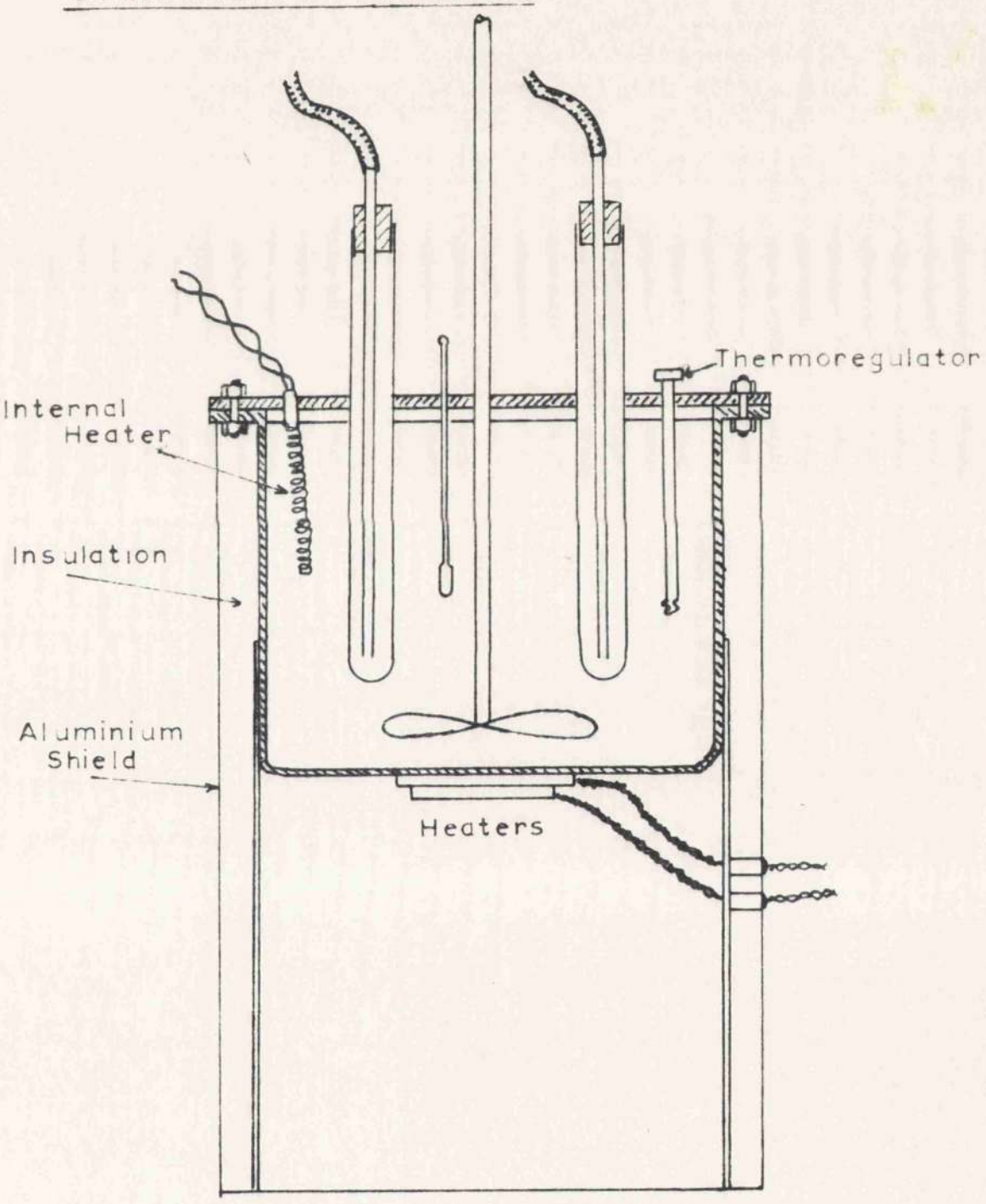
The test consists of passing air at 15 litres per hour through a 40 ml. sample of oil, in a boiling tube, kept at 200°C, for six hours, then leaving for eighteen to twenty-four hours and repeating for a further six hours to give a total oxidation time of twelve hours. Kinematic viscosity at 100°F and Ramsbottom carbon residue are measured before and after oxidation. The ratio of the viscosity after oxidation to the viscosity before, and the increase, on oxidation, of the percentage carbon residue are taken as measures of the deterioration of the oil.

The particular apparatus used is shown in Figure 8. Dimensions are according to specification. Heating is by means of two flat external heaters of 300 and 600 watts and one internal heater of 250 watts.

No.	Mol. Wt.	Visc. V_k	Analysis					Visc. Ratio	Carbon Residue %		
			C_p	C_N	C_A	R_N	R_A		Before	After	Increase
5	538	85.54	71.0	25.7	3.3	2.14	0.20	1.56	0.11	1.15	1.04
10	396	23.61	69.3	27.0	3.7	1.54	0.16	1.77	0.02	1.55	1.53
11	469	52.30	67.7	28.1	4.2	2.02	0.22	1.63	0.06	1.46	1.40
12	550	133.2	69.0	26.8	4.2	2.30	0.25	1.14	0.16	0.90	0.74
13	837	522.7	70.0	24.5	5.5	3.46	0.57	2.54	0.80	1.54	0.74
4	533	110.8	67.5	26.3	6.2	2.30	0.34	1.41	0.17	1.16	0.99
1	397	34.45	57.3	36.2	6.5	1.68	0.32	1.69	0.14	1.47	1.33
3	674	535.8	67.5	25.7	6.8	2.94	0.56	1.15	0.53	1.05	0.52
6	328	22.80	54.4	36.9	8.7	1.95	0.31	1.22	0.02	0.44	0.42
7	525	102.5	67.0	24.1	8.9	2.11	0.56	1.22	0.15	0.76	0.61
2	454	90.36	64.2	26.3	9.5	1.88	0.55	1.27	0.16	0.68	0.53
8	476	223.4	58.3	28.7	13.0	2.33	0.77	1.42	0.35	1.44	1.09
14	311	22.61	46.0	35.4	18.6	1.86	0.70	1.70	0.17	1.87	1.70
15	366	130.0	41.3	34.6	24.1	2.28	1.10	27.90	0.21	4.83	4.62
9	410	225.4	46.0	28.2	25.2	2.19	1.30	3.18	0.12	3.36	3.24
16	264	25.37	28.0	26.8	45.2	1.50	1.50	8.40	0.31	7.00	6.69
17	339	587.3	29.0	18.2	52.8	1.53	2.31	34.00	1.14	10.40	9.26

Table 9

OXIDATION APPARATUS



Scale-$\frac{1}{4}$ Full Size

FIG 8

Heating up from cold is carried out using the two large heaters, on control for safety. During operation the 300 watt heater, which is slightly less than required to balance the losses from the bath, is on continuously and the internal heater on control maintains the bath at 200°C.

Air is supplied by a small "Proctor" diaphram vibrating at mains frequency to give a non-pulsating air flow. Flow rates are measured by a U-tube flowmeter.

The apparatus is capable of taking four sample tubes and the procedure followed was according to specification.

Kinematic viscosity measurements at 100°F, before and after oxidation were measured as described on page 74 . The ratios of the viscosity before to that after oxidation gave the viscosity ratio.

The determination of the Ramsbottom carbon residue before and after oxidation to evaluate its increase was according to standard procedure I.P. 14/45 (38). The test estimates the percentage carbon residue remaining in a pyrex glass or silica bulb of specified dimensions after vapourisation of 1 to 4 gms. of oil at 550°C and the apparatus constructed (a lead bath) to take two bulbs is shown in Figure 9. The special arrangement of the lagging found necessary to obtain the required temperature is outlined.

RAMSBOTTOM APPARATUS

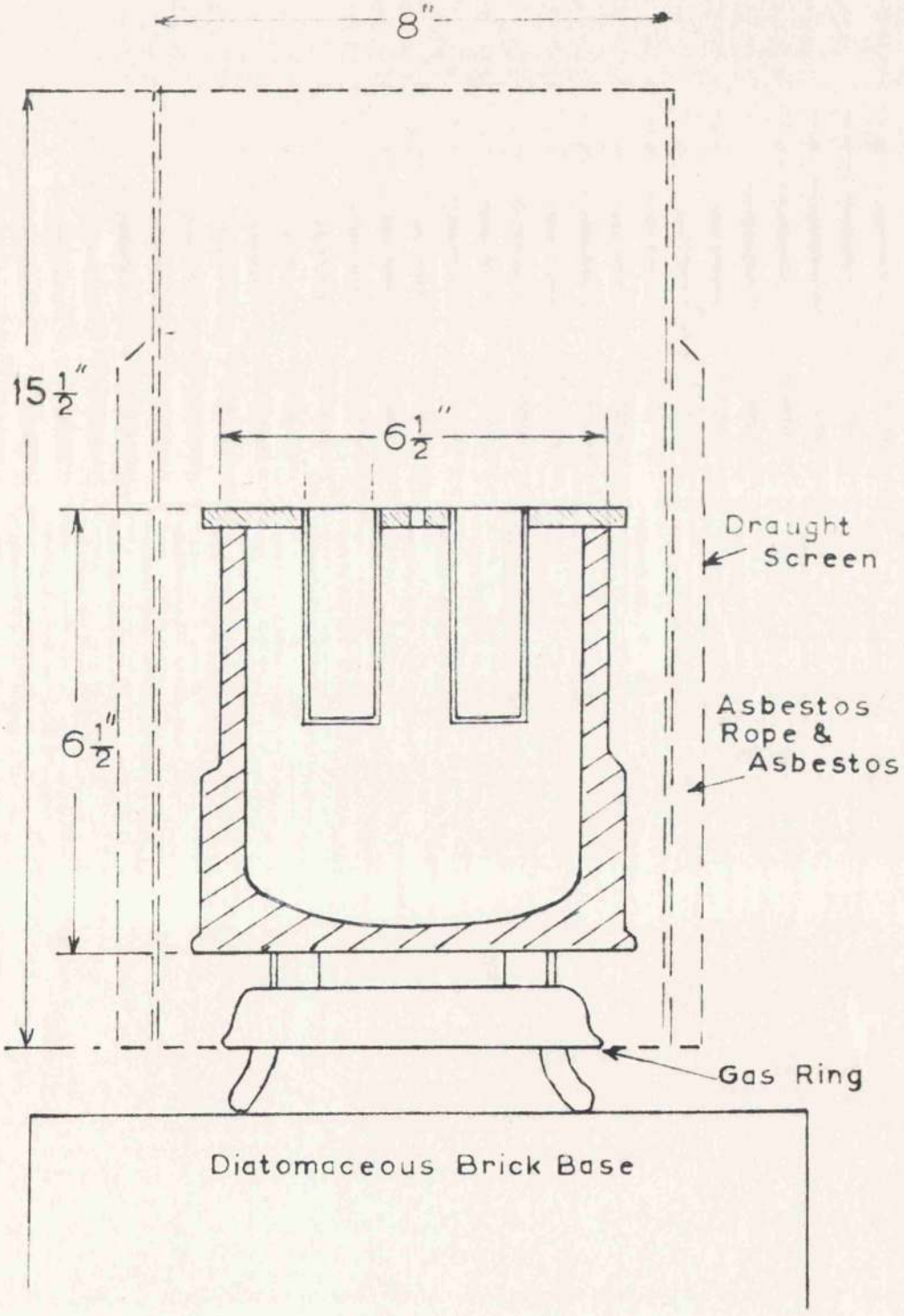
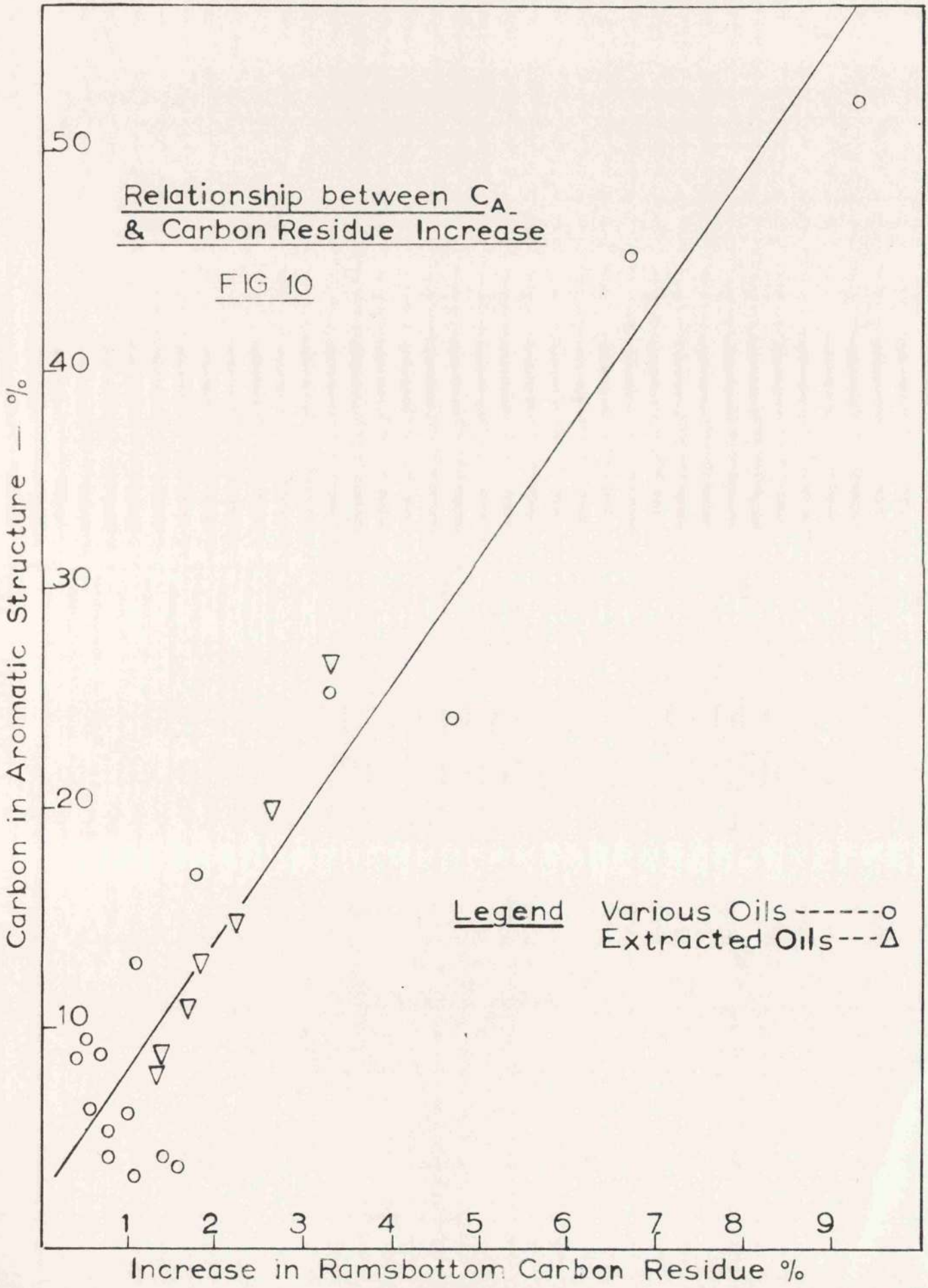


FIG 9


Relationship between C_A & Carbon Residue Increase
FIG 10
Carbon in Aromatic Structure — %
50
40
30
20
10
1
2
3
4
5
6
7
8
9
Increase in Ramsbottom Carbon Residue %
Legend Various Oils ------o
Extracted Oils ---Δ

Extration of a High Aromatic Oil

The results of the above work are discussed in detail later where it is concluded that aromatic content is one of the main factors in deterioration. However, in certain cases, and especially with the viscosity ratio measurements, no simple correlation is obtained with C_A or the other measured quantities. This is believed to be due to differences in molecular structure, i.e. whether non aromatic bonds are single or double, whether rings are condensed or not, etc.. It is also the only factor on which information was not obtainable.

It was felt that if the problem of molecular pattern could be kept constant and the aromatic content varied a clearer idea of the changes on oxidation would be obtained. Since molecular arrangement depends on the origin of the oil a series of samples were derived from one starting material.

This was done by the progressive removal of aromatics from an oil with C_A = 28% by extraction with a solvent to give a number of samples of varying aromatic content, which were then analysed and tested by the oxidation test.

Equal volumes (150 ml.) of high aromatic oil and furfural were shaken in a 500 ml. separating funnel and allowed to stand for three hours. The phases were separated by running off the extract. Solvent was removed from the extract by atmospheric distillation and recovered. Final traces were then removed by steam distillation using Youngsberg's test for traces of

furfural in aqueous solution (39). (Aniline and glacial acetic acid give a red coloration with traces of furfural in aqueous solution.). Water from the steam distillation was removed by ordinary atmospheric distillation. The extracts, viscous black materials, were retained for examination.

There was very little solvent in the raffinate and this was removed by steam distillation only. The raffinate provided oil lighter in colour than the starting material to give the second oil in the series.

By obtaining a raffinate similar to the above and taking it through the same process of extraction as the original oil the third member of the series was obtained.

Repetitions of the above techniques were carried out until seven oils in all were available, further extraction being unadvisable as the quantity of aromatics removed becomes ultimately so low as to be negligible.

The refractive indices, densities and kinematic viscosities were measured, at 20°C, on each of the samples and the results are as indicated below in Table 10.

Oil Sample	V_k	n	d
R0	1001.0	1.5278	0.9452
R1	781.8	1.5154	0.9300
R2	678.2	1.5085	0.9206
R3	611.7	1.5048	0.9151
R4	577.2	1.5024	0.9119
R5	537.8	1.5005	0.9094
R6	514.0	1.4989	0.9069
R7	499.6	1.4976	0.9050

Table 10

As can be seen above, these values, when examined, were found to be within the limits for the V_k-n-d analysis and this technique was, therefore, used. A correction was made for sulphur in the original oil, found to be 1.8%; in the others the content was negligible.

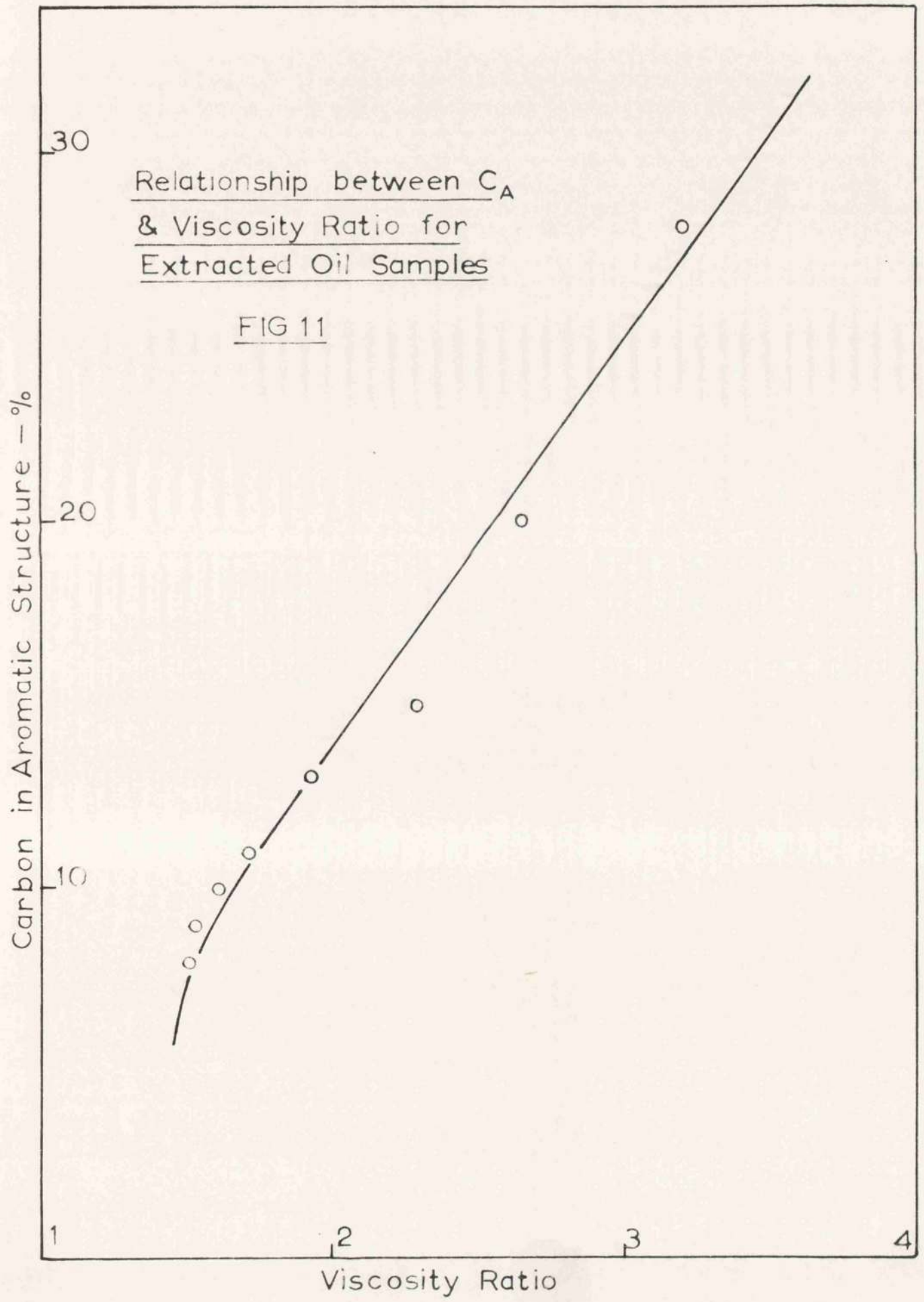
Oxidation tests were carried out on the series by the techniques already described. The results obtained are shown in Table 11.

The Ramsbottom carbon residue increases were plotted against C_A on the graph already drawn, Figure 10, for the various oils of different origin.

For each sample in the series viscosity ratio was also plotted against C_A. The result is shown in Figure 11.

No.	Mol. Wt.	Visc. V_k	Analysis by V_k-n-d					Visc. Ratio	Carbon Residue %		
			C_p	C_N	C_A	R_N	R_A		Before	After	Increase
RO	410	217.7	44.0	28.0	28.0	1.98	1.56	3.18	0.12	3.36	3.24
R1	435	185.2	48.0	32.0	20.0	2.42	1.03	2.65	0.10	2.66	2.56
R2	445	167.6	51.0	34.0	15.0	2.56	0.82	2.28	0.08	2.12	2.04
R3	445	157.1	52.0	35.0	13.0	2.64	0.70	1.91	0.06	1.88	1.82
R4	450	148.5	53.0	36.0	11.0	2.70	0.61	1.71	0.05	1.70	1.65
R5	450	143.1	53.0	37.0	10.0	2.74	0.54	1.60	0.04	1.56	1.52
R6	455	139.9	54.0	37.0	9.0	2.77	0.49	1.54	0.04	1.48	1.44
R7	455	136.8	54.0	38.0	8.0	2.79	0.46	1.50	0.03	1.42	1.39

Table 11


Relationship between C_A & Viscosity Ratio for Extracted Oil Samples
FIG 11
30
20
10
Carbon in Aromatic Structure – %
1
2
3
4
Viscosity Ratio

The Rate at which Oxygen is Absorbed in the Standard Test

It was of interest to measure the oxygen absorbed by an oil during the standard oxidation test. Figure 12 shows the apparatus.

The absorption cell was essentially a boiling tube with the cork, normally used, replaced by a ground glass joint sealed at the top. There was an air inlet tube. Both of these units awere constructed to the dimensions specified by the original test. In addition an outlet tube was fitted on top of the sealed joint.

Gases leaving the cell entered a water cooled condenser, fitted with a trap, a fog trap to remove fine mist and thence to an absortion train. In its final form this consisted of a ground glass stoppered U-tube filled with fine calcium chloride to remove water, a bubbler bottle filled with concentrated caustic soda which removed carbon dioxide and hydrocarbon gases, and a U-tube of coarse calcium chloride to deal with carry-over. A furnace tube filled with copper oxide converted any carbon monoxide to carbon dioxide and hydrogen to water and these were absorbed in a U-tube containing one limb of "ascarite" and one of calcium chloride. The circulation pump was placed after this U-tube.

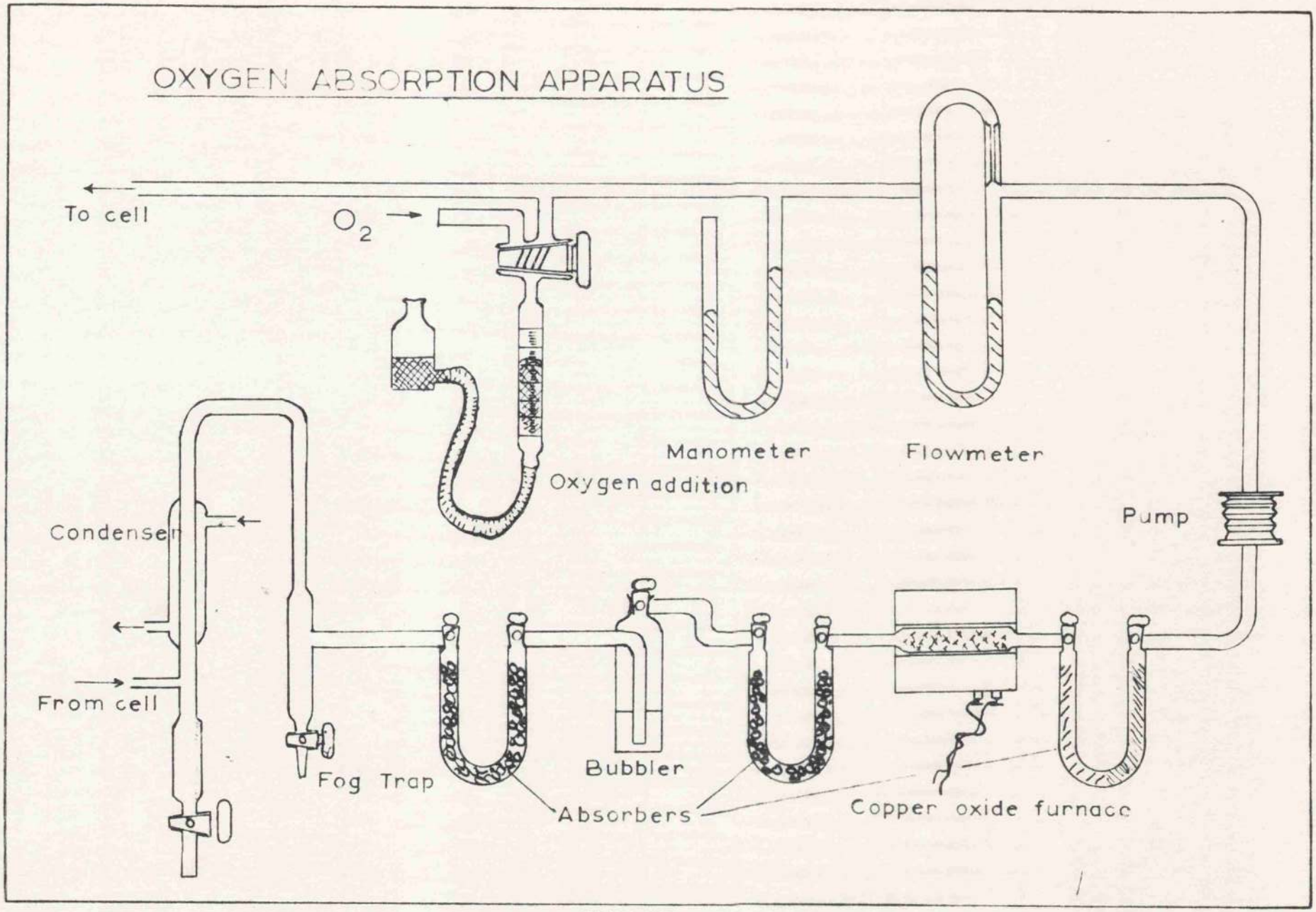

OXYGEN ABSORPTION APPARATUS
To cell
O_2
Manometer
Flowmeter
Oxygen addition
Pump
Condenser
From cell
Fog Trap
Bubbler
Absorbers
Copper oxide furnace

FIG 12

Air flow rates were measured on a water filled U-tube constriction flow meter and a water filled manometer measured pressure in the system.

Measured oxygen additions were made by the three way stop-cock shown, the settings of which were:- all entries and exits closed, flow of oxygen from a low pressure supply to a graduated measuring burette fitted with a mercury levelling bottle, and flow from the burette into the apparatus.

Circulation was effected by a diaphram pump, vibrating at mains frequency, with a specially constructed body and leak-proof diaphram. A drawing of the pump is shown, Figure 13. Bostic was used to seal the diaphram and on testing, the permeability of the rubber allowed no leakage.

Heating of the cell was carried out in the bath described for the standard test on page 81

Procedure

Before using the apparatus all ground glass joints and stoppers were coated with silicon stop-cock grease and the system tested for leaks by first running, without oil, under a few oms. water gauge pressure then under a few oms vacuum, until no pressure change was indicated in either case.

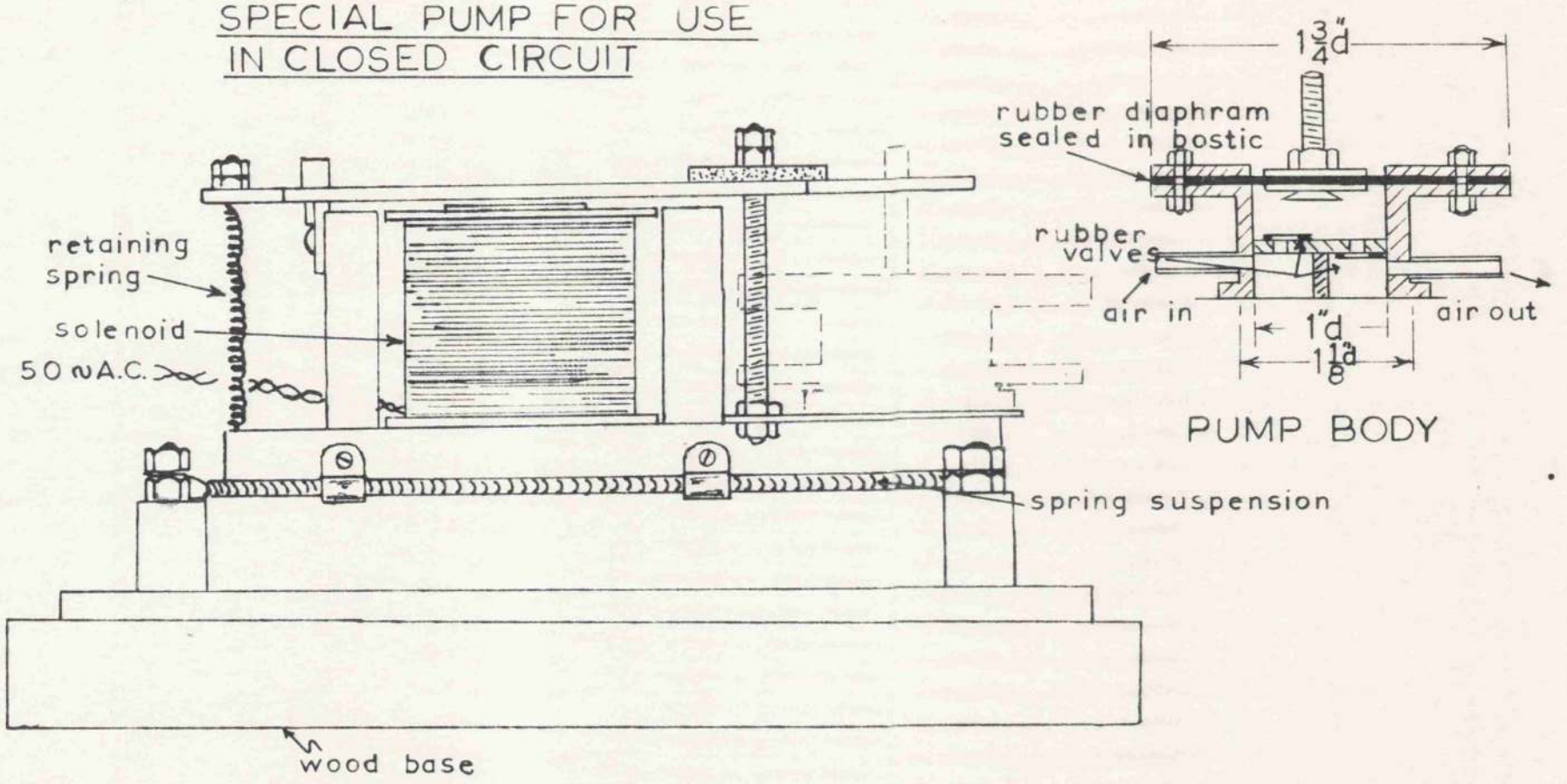

SPECIAL PUMP FOR USE
IN CLOSED CIRCUIT
retaining spring
solenoid
50 ω A.C.
spring suspension
wood base
1 3/4" d
rubber diaphram sealed in bostic
rubber valves
air in
air out
1" d
1 1/8" d
PUMP BODY
Scale - Full Size

FIG 13

When leak proof conditions were established 40 mls. of the oil to be tested were placed in the cell and allowed to reach 200°C in the heating bath for twenty minutes, when the cell was connected to the circuit.

At the start of a test the time was noted, the pump switched on, and the flow adjusted to 15 litres per hour. As oxygen was absorbed, indicated by a decrease in pressure, additions were made at time intervals dependent on the absorption rate for the sample being tested. All oxygen additions were measured at atmospheric pressure, the temperature noted and the volumes adjusted to N.T.P.

Considerable difficulty was found in obtaining absorbents capable of removing all the gaseous oxidation products. A number of tests were carrid out to find these.

Examination of Suitable Absorbents

All standardisation tests were carried out with one oil. Details are given of it below in Table 12

Sample Number	5
Refractive Index at 20 C	1.4803
Density at 20 C	0.8697
Molecular Weight	538
Kinematic viscosity of 20 C	235.3
Viscosity Index	

n-d-M analysis

C_A	3.3	R_A	0.21
C_N	25.7	R_N	2.14
C_p	71.0	R_T	2.35

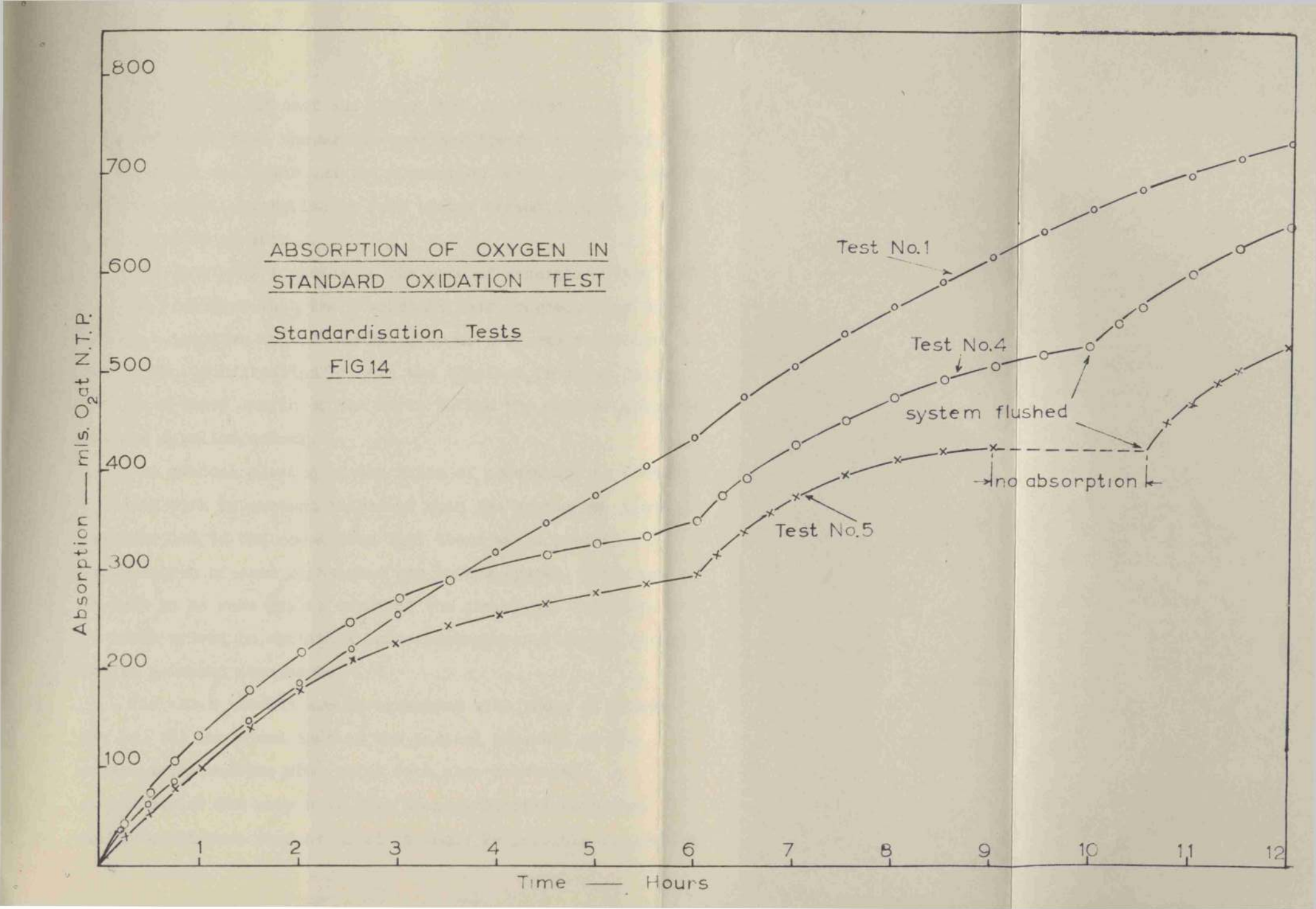
Each separate system of absorbents used with their position in the circuit is listed numerically in the text below.

(i) At first it was thought that water vapour, carbon dioxide and carbon monoxide would represent the bulk of the gas to be absorbed. The initial absorption train after the condenser and fog trap therefore consisted of a U-tube containing fine calcium sulphate, a U-tube of coarse calcium sulphate, a U-tube of ascarite (for CO_2), the furnace, and U-tube with one limb of ascarite and one of calcium sulphate.

Three tests each consisting of two six hour periods were carried out consecutively without changing the absorbents. The results are shown in Figure 14.

The first test showed a tendency for the rate, indicated by the slope of the absorption curve, to slow down as the test proceded. On restarting the second six hour period, a day later, when the circuit once again initially contained only air, the starting rate was higher than the final rate for the previous period. The tendency was again for the rate to fall away.

The second test showed the same general characteristics as the first but more defined as indicated by the pronounced peak at six hours. Since it was seen that at the start of a run, when only air was in the system, the rates were higher, it was decided to flush the system with air four hours after the start of the second period. As shown, the rate increased. The lower position of the curve on the graph indicated that the overall


ABSORPTION OF OXYGEN IN STANDARD OXIDATION TEST
Standardisation Tests
FIG 14
Test No.1
Test No.4
system flushed
no absorption
Test No.5
Absorption — mls. O_2 at N.T.P.
Time — Hours
800
700
600
500
400
300
200
100
1
2
3
4
5
6
7
8
9
10
11
12

rate for the second test was lower than the first.

The third test showed the previous trends to continue. The overall rate was lower and the absorption rates decreased as the test proceded, absorption in fact having ceased during the second period of test.

The continual lowering of the rate of absorption from test to test indicated that the absorbents were progressively being rendered inactive by the organic gaseous products formed on oxidation. Confirmation of this was obtained from the fact that in a short length of the first U-tube the calcium sulphate assumed a yellow colour.

The gradual slowing of the rates of absorption as a test proceded with subsequent increases when the system was flushed with air led to the conclusion that there was a gradual accumulation of some unabsorbed gas in the system. This was thought to be same gas as rendered the absorbents inactive, but it later proved to contain a large percentage of carbon dioxide due to poisoned absorbent.

The above results are in agreement with those of Dornte (9, 15, 16) who found that as the partial pressure of the oxygen decreased the absorption rate also decreased.

Study of the graphs at this stage indicated that when normal conditions were attained it would be possible to predict

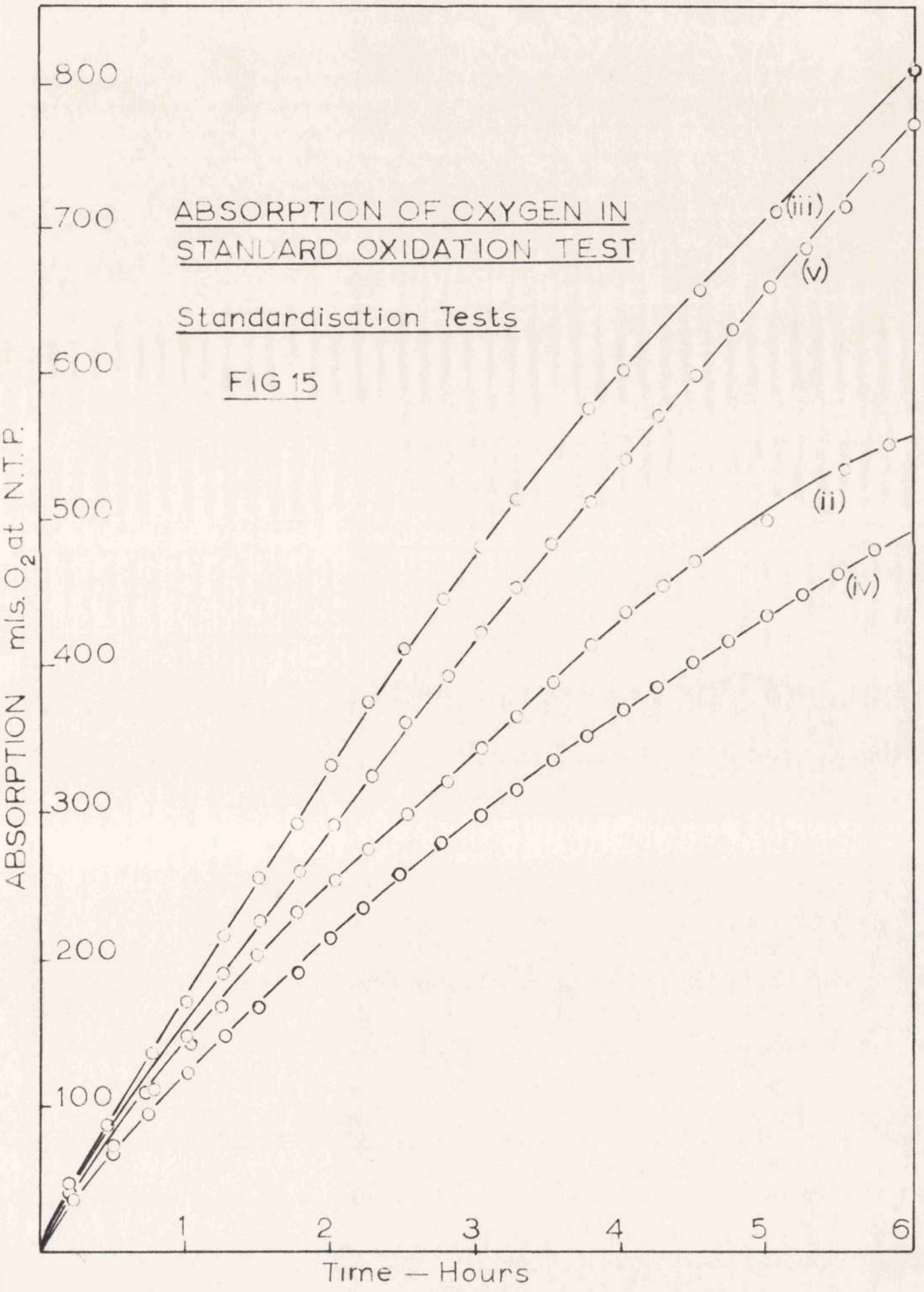
the twelve hour absorption figure from a six hour test. Subsequent tests were, therefore, made over six hours.

(ii) Efforts were now directed towards removing the organic gas poisoning the absorbents. Two methods were considered, activated charcoal as an absorbent and a freezing trap.

In the second U-tube the calcium sulphate was replaced by activated charcoal and a six hour test carried out. The absorption curve is shown in figure 15. At the end of this test it was decided to analyse the gas in the circuit using a Hempel gas analysis apparatus and it was found to contain 14% carbon dioxide showing the ascarite absorption to be poisoned.

(iii) To remove carbon dioxide a bubbler bottle of concentrated caustic soda replaced the activated charcoal followed by a drying agent. At this stage the more efficient drying agent calcium chloride was used to replace the calcium sulphate.

This test gave a higher absorption rate than any previous test, a gas analysis indicated an oxygen content in the region of 20% at the end of six hours and flushing the system with air produced no change in the absorption rate. The indications, therefore, were that all gaseous products were removed by the caustic soda, originally intended to remove carbon dioxide. Confirmation of this existed in the deep yellow discoloration of the solution and the formation of dark brown residues in the bubbler.


ABSORPTION OF OXYGEN IN
STANDARD OXIDATION TEST
Standardisation Tests
FIG 15
ABSORPTION mls. O_2 at N.T.P.
800
700
600
500
400
300
200
100
1
2
3
4
5
6
Time — Hours
(iii)
(v)
(ii)
(iv)

The above was later to be taken as the final absorption. system.

(iv) On reverting to the original system and a freezing trap, of solid carbon dioxide in acetone, low rates were again obtained Figure 15. It would appear that the retention time in the freezing trap was too low to condense everything.

(v) A repeat test with the finalised absorption train gave reproducible results as shown.

Absorption Rate Studies

Six hour absorption tests were carried out on eight samples of lubricating oil fractions. The molecular weights and percentages of carbon in aromatic structure, C_A, for each sample are given in Table 13. Full details and n-d-M analysis for each oil is given in Tables 1 and 2. The absorption curves are shown in Figure 16.

Rate of Change of Physical Constants with time of Oxidation

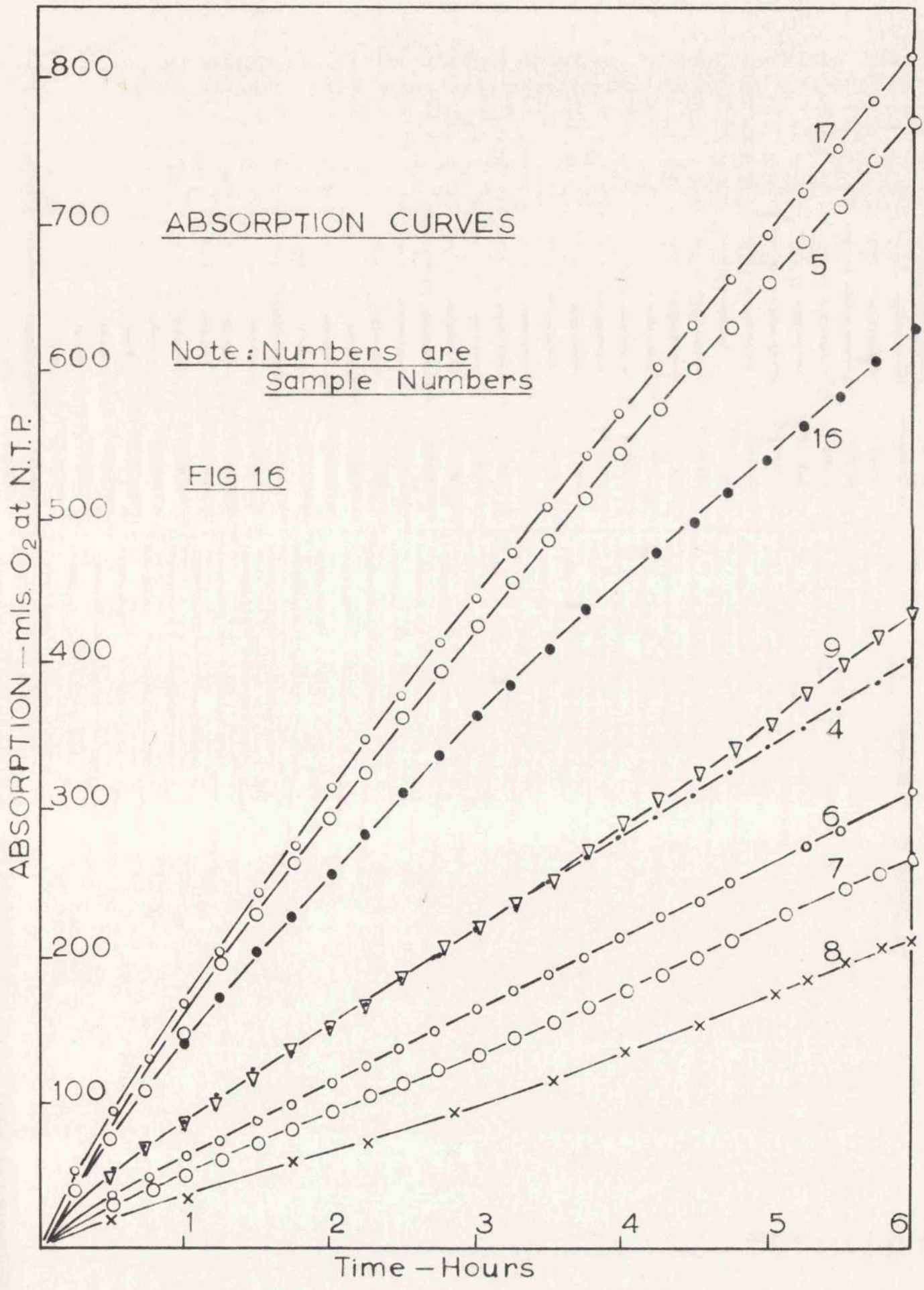
Four selected oils were progressively oxidised and the nature of the changes in a number of constants examined. Complete analyses of the samples were available from the earlier work.

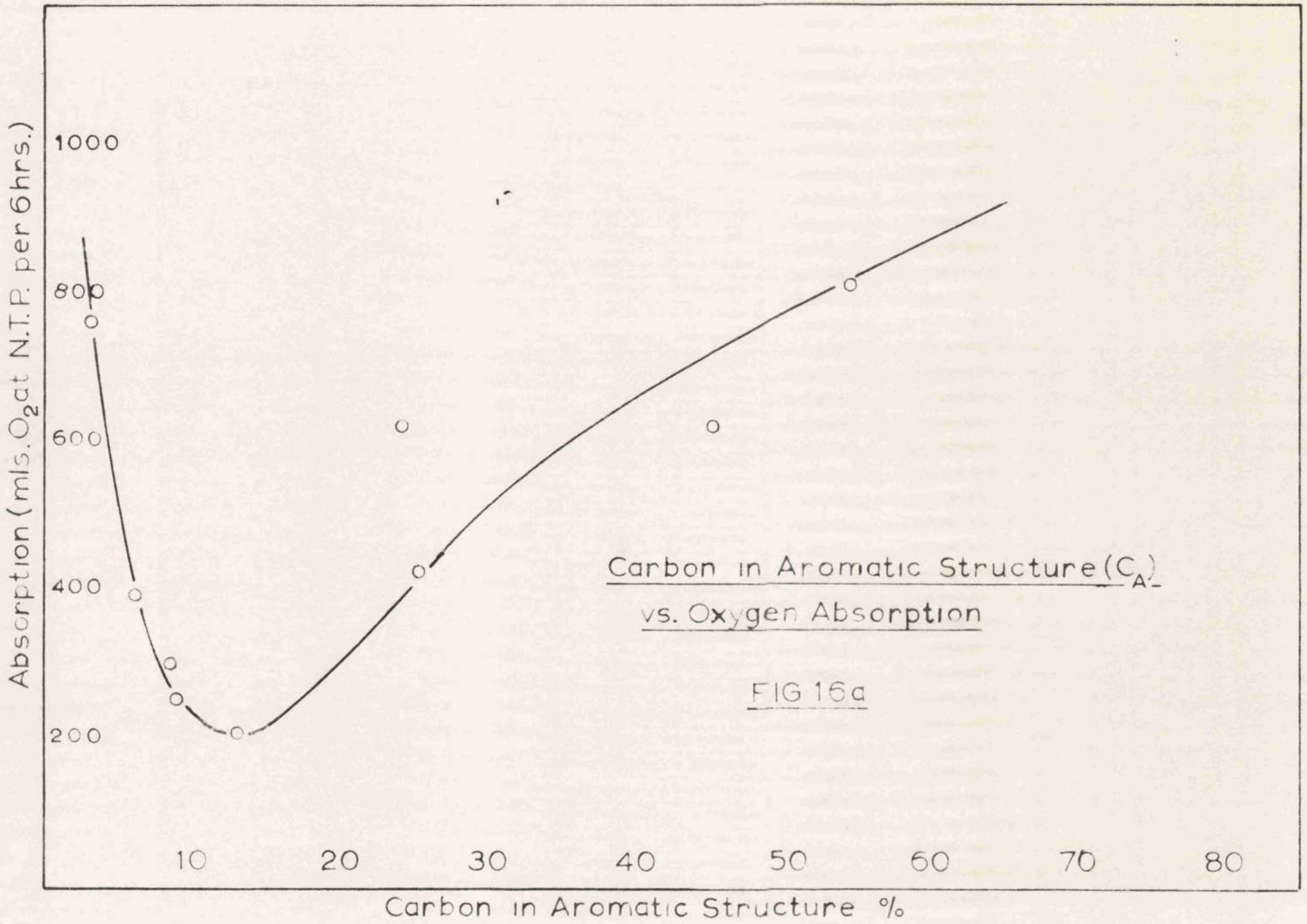
Procedure

Four refined lubricating oil fractions were chosen, three of low aromatic content (less than the critical value of 10% of the carbon atoms in aromatic structure already referred to) but of widely different molecular weights, and the fourth of high aromatic content.

Sample No.	Mol. Wt.	C_p	C_A	C_N	R_A	R_N
5	538	71.0	3.3	25.7	0.21	2.14
4	533	67.5	6.2	26.3	0.34	2.30
6	328	54.5	8.7	36.9	0.31	1.95
7	525	67.0	8.9	24.1	0.56	2.11
8	476	58.3	13.0	28.7	0.77	2.33
9	410	54.0	25.2	28.8	1.30	2.19
16	264	72.0	45.2	26.8	1.50	1.50
17	339	71.0	52.8	18.2	2.31	1.53

Table 13


ABSORPTION CURVES
Note: Numbers are Sample Numbers
FIG 16
ABSORPTION — mls. O_2 at N.T.P.
Time — Hours
800
700
600
500
400
300
200
100
1
2
3
4
5
6
17
5
16
9
4
6
7
8



Carbon in Aromatic Structure (C_A) vs. Oxygen Absorption

FIG 16a

A summary of the analysis and other pertinent data relating to the oils used appears below in Table 14

Sample No.		Mol. Wt.	C_P	C_A	C_N	R_N	R_A
Low. Aromatic	1	397	57.3	6.5	36.2	1.68	0.32
	2	454	64.2	9.5	26.3	1.88	0.55
	3	674	67.5	6.8	25.7	2.94	0.56
High Aromatic	16	264	28.0	45.2	26.8	1.50	1.50

Progressive oxidation of these samples was carried out using the apparatus of the standard oxidation test (38). The test specified that air at a rate of 15 litres per hour be passed through 40 ml. of oil in a boiling tube kept at 200°C for two six hour periods to give a time of oxidation of twelve hours. In this work all conditions were as specified, except for the time of oxidation, which was varied from 0 to 12 hours. Oxidation times exceeding six hours were carried out in two stages on consecutive days.

For the four series of oxidised oils obtained densities, viscosities, viscosity indices and surface tensions were measured. Ramsbottom carbon residues were determined for the series derived from sample No. 1.

A summary of the analysis and other pertinent data relating to the oils used appears below in Table 14.

Sample No.		Mol. Wt.	C_p	C_A	C_N	R_N	R_A
Low. Aromatic	1	397	57.3	6.5	36.2	1.68	0.32
	2	454	64.2	9.5	26.3	1.88	0.55
	3	464	62.5	6.8	25.7	2.94	0.56
High Aromatic	16	264	28.0	45.2	26.8	1.50	1.50

Progressive oxidation of these samples was carried out using the apparatus of the standard oxidation test (38). The test specified that air at a rate of 15 litres per hour be passed through 40 ml. of oil in a boiling tube kept at 200°C for two six hour periods to give a time of oxidation of twelve hours. In this work all conditions were as specified, except for the time of oxidation, which was varied from 0 to 12 hours. Oxidation times exceeding six hours were carried out in two stages on consecutive days.

For the four series of oxidised oils obtained densities, viscosities, viscosity indices and surface tensions were measured. Conradson carbon residues were determined for the samples derived from sample No. 1.

Densities were measured at 20°C in thermostated water baths. A calibrated specific gravity bottle was used for the series from sample No. 1 and the errors arising from the oil trapped in the ground glass stopper were evident when density was graphed against time of oxidation, Figure 17. Subsequent measurements were by the U-tube pycnometer method evolved and described in detail earlier. The values obtained were also plotted on Figure 17.

Viscosities were measured in centistokes according to the Institute of Petroleum specification I.P. 71/47 using calibrated Oswald U-tube viscometers in a thermostated water bath as described on page 74 at a temperature of 100°F. Values obtained were plotted in semi-logarithmic co-ordinates to a base of oxidation time. These appear in Figure 18.

Viscosity measurements at 210°F gave the viscosity index according to the Institute of Petroleum specification. Table 15 shows the results.

Surface tensions, in dynes per cm., at 20°C were measured by Sugden's bubble pressure method, described by Findlay(40). For reasons described later only a few results have been recorded. These are in Table16.

The Ramsbottom carbon residue determination is a purely empirical test but as its increase on oxidation is one of the quantities required in the standard oxidation test the nature of its change during oxidation for one series (Sample No. 1) of oxidised samples was determined. The test was carried out according to the Institute of Petroleum specification I.P.14/45 and the results obtained - increase in carbon residue - plotted to a base of time of oxidation of the sample as shown in Figure 19.

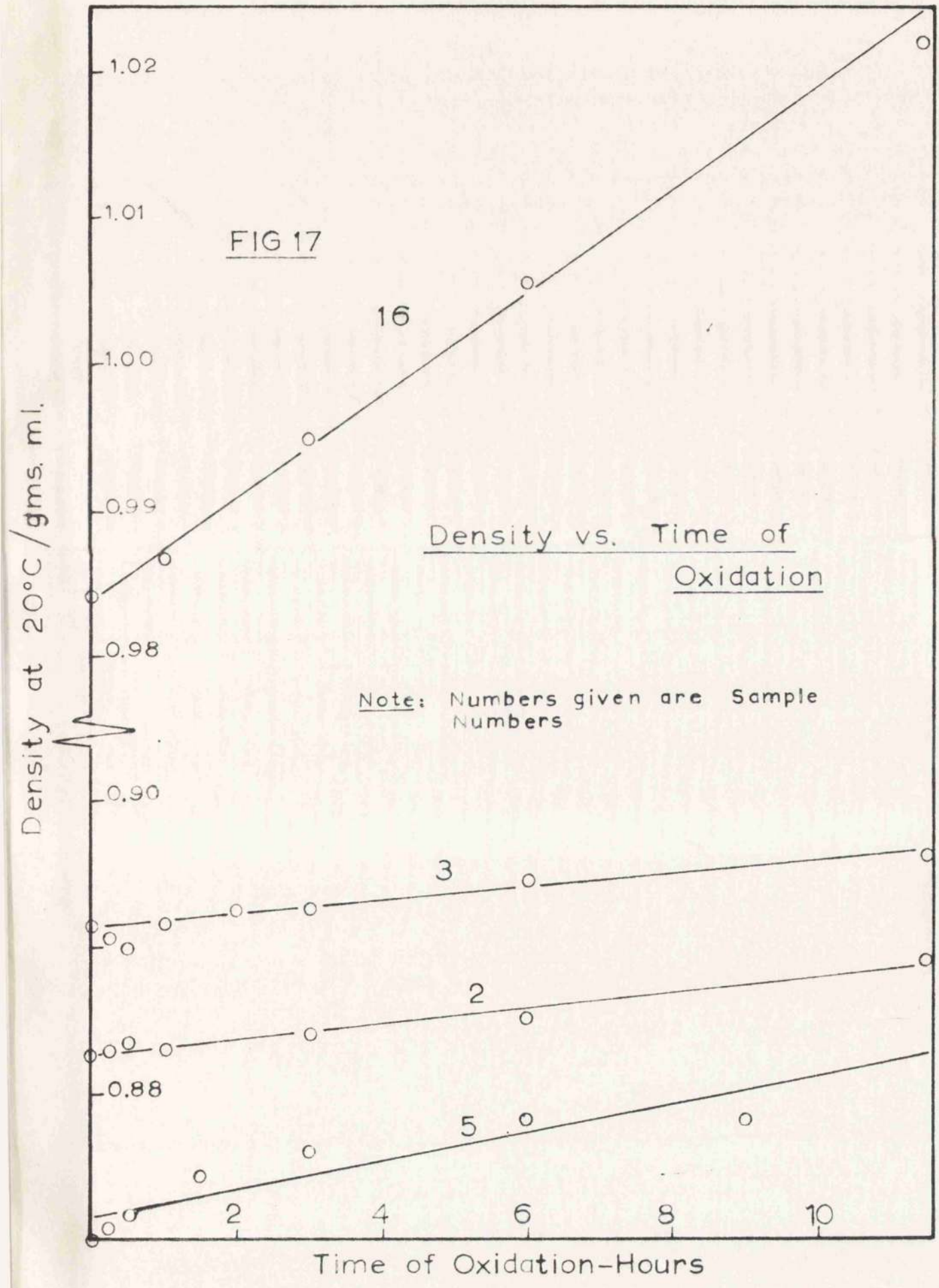


FIG 17
Density vs. Time of Oxidation
Note: Numbers given are Sample Numbers
16
3
2
5
1.02
1.01
1.00
0.99
0.98
0.90
0.88
2
4
6
8
10
Density at 20°C /gms. ml.
Time of Oxidation-Hours

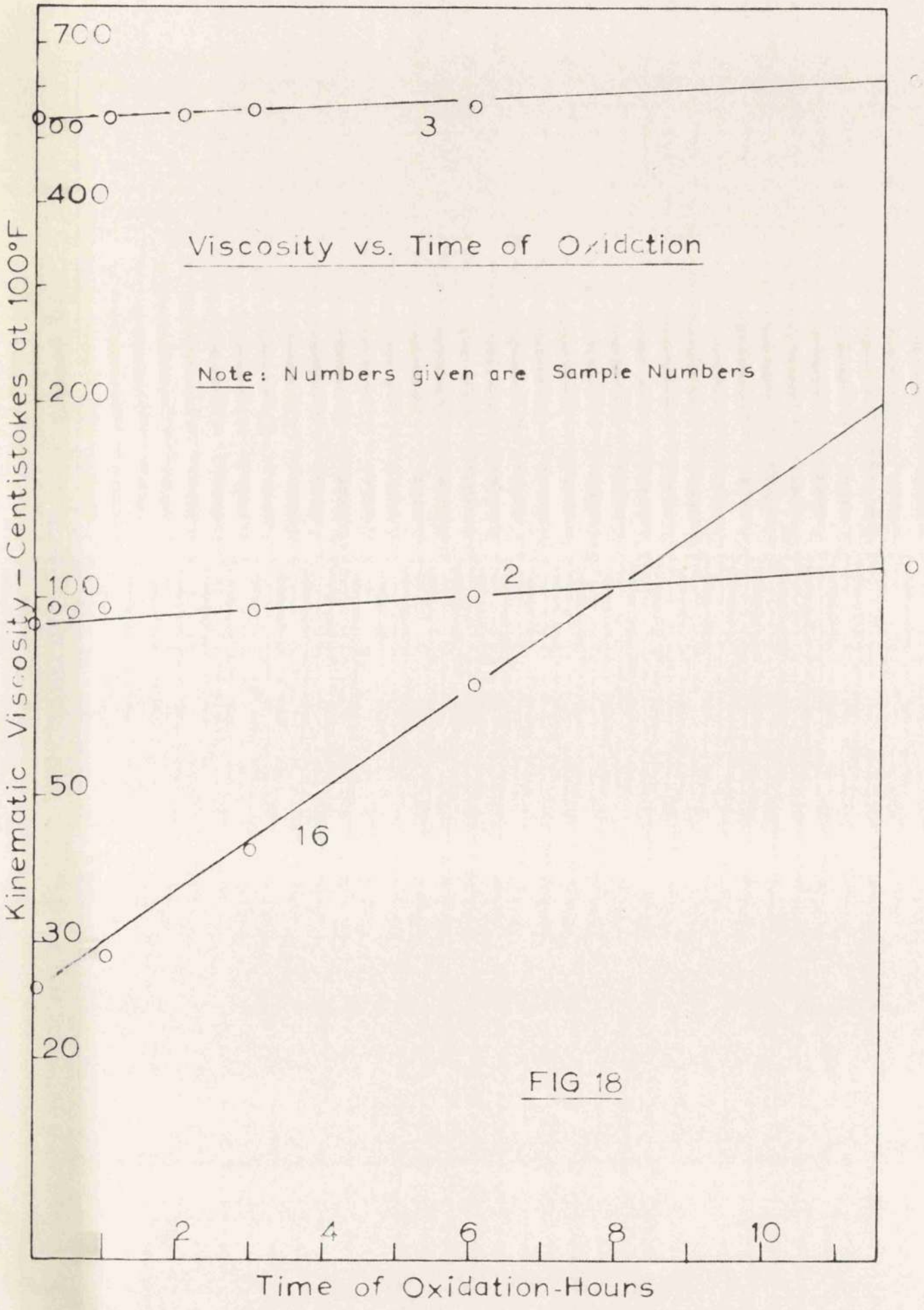

Viscosity vs. Time of Oxidation
Note: Numbers given are Sample Numbers
Kinematic Viscosity – Centistokes at 100°F
700
400
200
100
50
30
20
3
2
16
2
4
6
8
10
Time of Oxidation-Hours

FIG 18

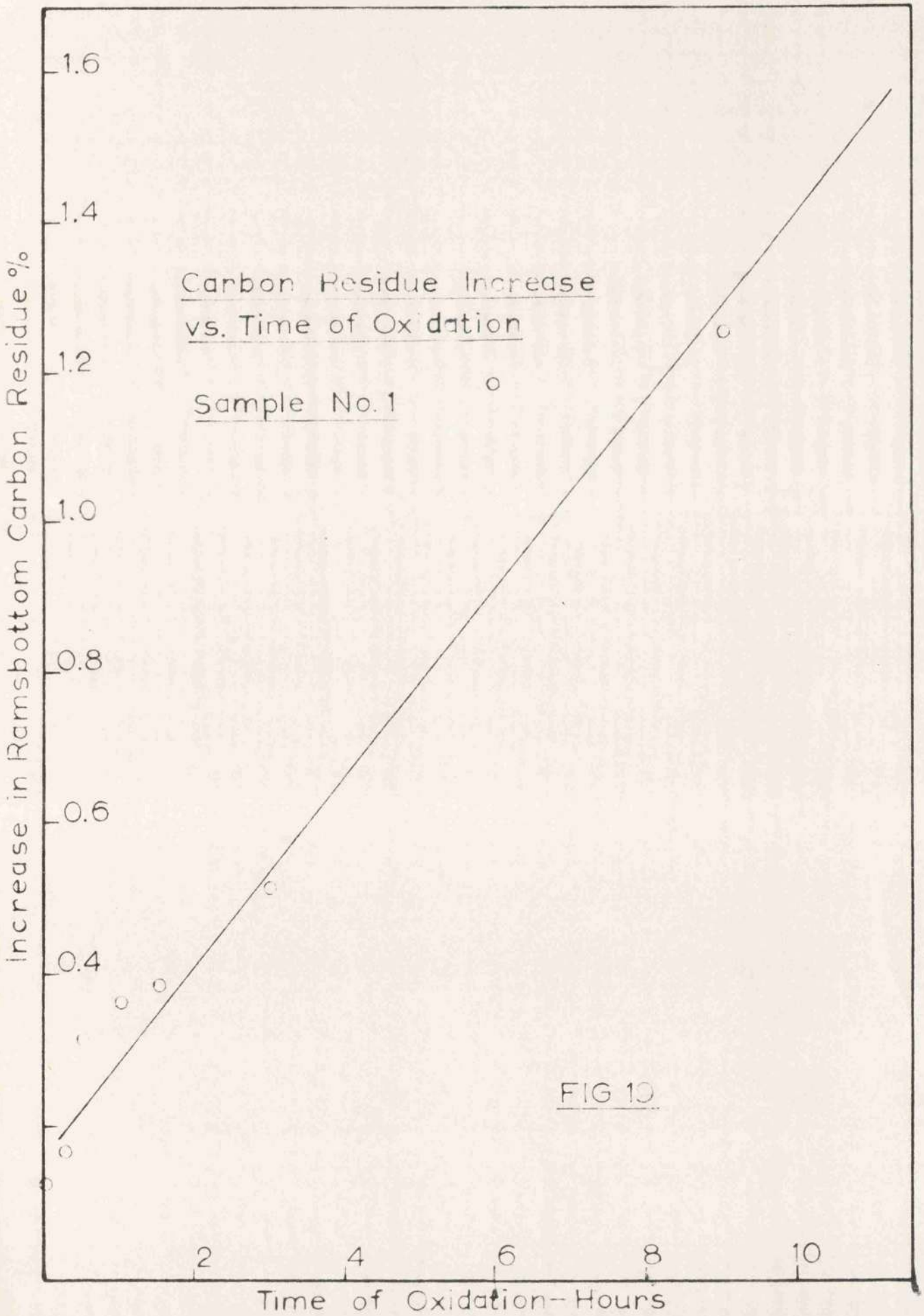

Carbon Residue Increase
vs. Time of Oxidation
Sample No. 1
Increase in Ramsbottom Carbon Residue %
1.6
1.4
1.2
1.0
0.8
0.6
0.4
2
4
6
8
10
Time of Oxidation – Hours

FIG 10

Discussion of Results

The following discussion is in three parts each relating to the various types of tests carried out.

Effect of Molecular Structure on Oxidation Test Results

The results for the normal oxidation tests with the oil analysis figures for the seventeen samples are shown in Table 9 As established by other workers aromatic content is a significant factor in deterioration. Results are consequently tabulated in order of increasing percentage carbon in aromatic structure C_A.

The first general indication is that below a value of C_A = 10% there are no definite trends in the viscosity ratio and carbon residue increase. However, above this value both factors increas markedly with increasing C_A. Respective values at C_A = 9.5 are 1.27 and 0.53%, whereas at C_A = 52.8 are 34 and 9.26%. This would indicate that at high aromatic levels C_A is the principal controlling factor, and that a change in the nature of oxidation takes place at about C_A = 10.

It was not expected that the results could be expressed graphically as many factors besides aromatic content varied from sample to sample (molecular weight, nature of carbon bonds, etc.). This was found to be the case with viscosity ratio. However, by plotting C_A and carbon residue increase a direct relationship was indicated. Figure 10 shows this. At values of

C_A less than 10% a scatter of points within a narrow carbon residue band is shown.

It may be concluded frpm the foregoing that above the critical value of C_A = 10% the oxidised products are formed from the aromatic portion of the oil, whereas when C_A is less that this value are mainly derived from the saturated element (naphthenic and paraffinic). Since aromatic products are less volatile and more residue forming in nature this explains the relationship between carbon residue increase and C_A in the upper aromatic range.

In the lower aromatic range the indefinite and low results may be attributed to the fact that the oxidised saturated compounds are more volatile and are mostly vaporised in the carbon residue test but those which do form residues are mixtures of products derived from naphthenic and paraffinic hydrocarbons, each with its own characteristic residue weight, in proportions depending on the original oil.

The above also explains the viscosity ratio results, oxidised aromatics being more viscous than oxidised paraffins and naphtheness. Lack of correlation may be due to the fact that all oxidised products are still present in the oil during a viscosity measurement while during a residue determination oxidised saturated material is mainly vaporised.

Since the fractions tested represent a heterogeneous collection of refined oils of different geological origin, the order of magnitude of the increase of carbon residue on oxidation should be predictable if C_A is known.

The results for similar tests on the series of extracted oils are showin in Table 11.

When results for carbon residue increase are plotted on the graph already drawn, Figure 10, the curve coincides with that already obtained confirming what has been said.

With the series of extracted oils a correlation is now apparent between viscosity ratio and C_A as shown in Figure 20. It is interesting to note that at values of C_A less than 10% the graph tends to fall towards the viscosity ratio axis. This would confirm that below this figure compounds of a different and less viscous nature are formed but above the compound are the more viscous type derived from aromatics.

It is also noted that if the linear portion of the graph were produced it would pass through unity on the viscosity ratio axis. This would indicate that if the oxidation of aromatics was not replaced by oxidation of mainly saturated compounds the viscosity would not increase when an oil of zero aromatic content were oxidised.

Effect of Molecular Structure on Oxygen absorption Rate

Details relating to the samples on which absorption tests were carried out are given in Table 13 and the absorption curves are shown in Figure 16.

All graphs, except for the initial induction period at the start, are linear or almost linear, i.e. oxygen is absorbed at a constant rate.

Dornte (9, 15, 16) states that three types of absorption curves are obtained, depending on the product being oxidised; i) Autocatalytic where the rate increases with time; ii) Linear where the rate is constant and; iii) Autoretarded where the rate decreases with time.

Other workers show similar results or curves which are for part of the time of one type and partly the other. In all three cases, however, oxidation was much more severe, the cells normally having sintered glass bases, to give intimate contact between gas and oil, and using pure oxygen. In the present work the absorption is equivalent to only a very short oxidation time, and the curves will therefore be necessarily linear.

The order of magnitude of various factors in the standard oxidation test are derived from the results obtained. For the oils tested th e maximum rate of absorption of oxygen was 135 ml. measured at N.T.P., per hour, the minimum 35 ml. per hour.

The total absorption which could be expected in the standard test is obtained by increasing the six hour absorption by a factor of two and is seen to vary from 420 ml. of oxygen at N.T.P. to 1640 ml. for the particular fractions investigated.

The influence of aromatics has again been studied. No correlation is apparent until C_A is graphed against absorption after six hours (a factor which is proportional to the rate of absorption) when a curve of the type shown in Figure 16A is obtained. This indicates that at low values of C_A, absorption is very high, decreasing to a minimum at approximately 10% C_A, then increasing with increasing percentage carbon atoms in aromatic structure.

In the previous section it was shown that above a value of C_A of approximately 10%the increase in Ramsbottom carbon residue on oxidation was proportional to C_A while below this value a scatter of results around a mean value was obtained. Similar but less definite results were given for the viscosity ratio. At this point it had been assumed that these effects were related to the formation of non-volatile residue-forming products above the critical value of C_A. On the other hand, below the critical value the saturated hydrocarbons were oxidised to give more volatile products.

In the present section a definite change in the nature of the oxidation-absorption mechanism is seen at C_A = 10%.

This confirms that two different processes are taking place and the change from one to the other occurs at the same value of C_A in both investigations.

Denison (10) states that, when using pure compounds, both saturated hydrocarbons and aromatics are extremely stable to oxidation as indicated by absorption tests, but mixtures of these are extremely unstable. Booser and Fenske (41) confirm that pure aromatics are stable but in mixtures appear to be preferentially oxidised. It seems, therefore, that one type of hydrocarbon acts as a catalyst for the oxidation of others. Therefore, if it is assumed that (i) in the case of low aromatics (oils containing less than critical value) these catalyse the oxidation of saturated hydrocarbons, and (ii) in the case of high aromatics (above critical value found) that the oxidation of these is catalysed by the saturated hydrocarbons, irrespective of the amount of catalyst present in each case, an explanation of the results of the present investigation is obtained, i.e. in (i) absorption is dependent on the preferential oxidation of saturated hydrocarbons only and in (ii) on the preferential oxidation of aromatics only 10% C_A or 90% saturated hydrocarbons representing the critical value where change over takes place.

As with the previous investigation, the samples used here represent a heterogeneous selection of diverse origins and the results should therefore be general. Due, however, to the

complexity of oil oxidation they cannot be expressed mathematically.

One of the complexities is the role of the naphthenic and paraffinic constituents which have been considered collectively as saturated hydrocarbons. As the ratio of these two alter it is expected that the course of the oxidation will also alter but indications from examination of Tables 5 and 6 are that the effect is slight compared with that of aromatics. The same conclusion may be stated when molecular weight is considered.

The only sample containing appreciable sulphur was sample No. 9. Denison (10) states that sulphur is a definite inhibitor. This could explain the lower absorption than sample 16 which is of almost the same aromatic content.

In reviewing literature on absorption, Diamond, Kennedy and Larsen (42) indicate that absorption of oxygen does not depend on the bulk of the oil present, but only on the area exposed to the oxygen. This indicates a defect in the standard oxidation apparatus and absorption cell used where the area of oil in contact with air varies as the bubble size emerging from the air inlet tube. This will be a function of the surface properties of the oil.

Effect of Oxidation Time on Physical Properties of Oils

Work on viscosity often indicates that the logarithm is additive. Viscosities have, therefore, been plotted against a logarithmic scale.

Density and viscosity when plotted to a base of time of oxidation show, in all cases, linear relationships. Density correlations are shown in Figure 17 . The rates of increase of this factor, for the three oils in the low aromatic range are, as can be seen, of the same order and relatively low (0.00042, 0.00045 and 0.00098 units per hour) with a tendency for the rate to increase as the molecular weight decreases. The sample in the high aromatic range shows a much increased rate (0.00317 units per hour).

Similar characteristics to density are shown by the logarithm of viscosity in Figure 18 . The three low aromatic oils giving gradients of the same order, with a tendency to increase as the molecular weight decreases and the high aromatic oil giving a graph of markedly increased gradient.

The relationship for the density of a liquid resulting from the mixing of two liquids of dissimilar density, assuming no volume change on mixing, shows that density is in this [redacted] additive, i.e. if x parts, where x is small in

relation to unity, of a liquid of density D_C is added to unit volume of liquid of density D, the resulting liquid will have a density D_M given by

$$D_M = D + xD_C$$

or the resulting density is a linear function of x. Comparing this with the relationship obtained in Figure 17 the oxidation process studied can be regarded as equivalent to the regular addition with time of limited quantities of a liquid of higher density.

It was found previously that the oxygen absorbed was directly proportional to time of oxidation. Since it may be assumed that a constant proportion remains in the oil in the form of oxidised hydrocarbons, it is evident that the density is directly proportional to the oxygen in the form of oxidised products in the oil. From this it may be deduced that each ml. of oxygen entering the oil forms a definite amount of oxidised products or products of characteristic density, and these do not change markedly during the whole course of the oxidation test.

If the density function is replaced by the logarithm of viscosity, the same equation holds for the viscosity of a liquid formed by the mixing of two liquids of different viscosity.

Parallel conclusions can, therefore, be drawn for the oxidation process when viscosity is considered.

The more dense and viscous nature of the products formed on oxidation of high aromatic oils is seen from the above deductions and Figures 17 and 18. A further contributing factor is possibly that more of the products formed remain in solution in the oil.

The table of viscosity indices, Table 5, shows that in all cases there is no significant change in the viscosity temperature relationship for the oils on oxidation within the maximum time of oxidation used. In general when the oils are oxidised both the high and the low viscosity points rise simultaneously and proportionately.

Although the surface tensions of the oil samples cover a range of values, oxidation would appear to have little effect on the result. Complete results are, therefore, shown for one series only, in Table 16.

The empirical nature of the Ramsbottom carbon residue test gives a graph, Figure 19, which tends to be linear but could also be shown to have a rate which decreases with time.

Time of Oxidation - hours	Viscosity Indices			
	1	2	3	16
0	+101	+101	+94	-120
¼	+97	+107	+96	
½	+98	+103	+98	
1	+92	+101	+95	-124
1½	+91			
2			+97	
3	+96	+102	+95	-125
6	+100	+102	+96	-70
9	+100			
12		+100	+95	-75

Table 15

Oil Sample	Surface Tension dynes/cm. at 20°C
Sample II	
0	36.45
¼	38.25
½	38.17
1	38.34
3	37.27
6	38.84
12	38.27
Sample I	42.96
Sample XVI	38.85

Table 16

Effect of Oxidation on Lubricating Properties of Oil

The following section deals with the changes in the lubricating and mechanical properties of oil fractions in the course of oxidation in the standard oxidation test (38). Three types of test apparatus have been used.

The Avery Brownsdon Machine

The modified Avery-Brownsdon machine used in this investigation measures wear and oil film pressure characteristics of oils.

In its original form the machine carries out a type of wear test first described by Brownsdon (43). A one inch diameter hardened steel wheel, 0.1 inches thick, with a 0.05 inch radius on the periphery, rotates against a flat, oil lubricated specimen of bearing metal, held against it underload, to produce an elliptical scar. The length of the major axis of the scar after running for fifteen minutes at 500 r.p.m. with a load of 20 lbs. is taken as a measure of the wear.

In its present form the machine has been adapted to perform a test first used by Jannin (44) and described by Connelly (45). It uses a one inch diameter wheel, half inch in breadth, rotating against a one tenth inch wide flange of a specimen of bearing metal made to the dimensions show in Figure 23. The bearing metal is held to the rotating wheel under load to produce a cylindrical impression with wear. Provision for measuring the depth of impression enable a curve of wear against time to be plotted.

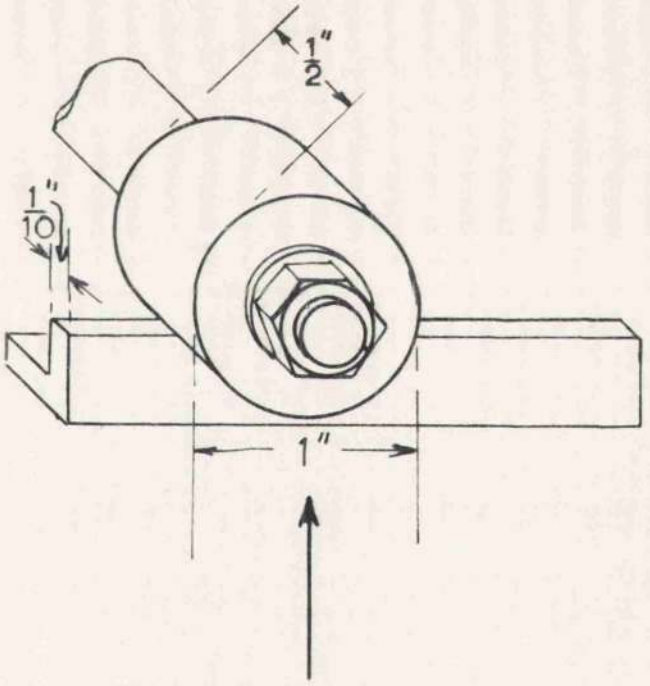
As the projected area of the scar is continually increasing and the force between specimen and wheel is constant so the pressure between the rubbing surfaces is continually decreasing. According to Connelly, the principle will record "wear under service conditions and rate of wear at different pressures".

Normally the Avery Brownsdon machine is used to test bearing metals and factors such as the nature of the wheel used, its surface finish, speed, load, oil used and its rate of feed are important. Here the machine is employed to test deteriorated oils. Consequently in any one series of tests all the above except the lubricating medium are kept constant and in the complete investigation the only factor which has been changed is the bearing metal material.

A photograph of the modified test unit is shown in Figure 24. The hardened wheel is driven from a V-belt pulley by a $\frac{1}{4}$ h.p. electric motor. Speed control is by a rheostat in the motor circuit and a revolution counter enables the speed to be checked.

The specimen of bearing metal is clamped to a table which is free to move in a vertical direction and the force between specimen and wheel is provided by a lever arm and weights, parallel to the wheel axis. Figure 23 shows the arrangement. A hand lever, with a locking position (load off) enables the table and speciment to be brought up and into contact with the wheel, gradually, to prevent shock loading and deformation of the bearing metal.

PRINCIPLE OF MODIFIED
AVERY BROWNSON MACHINE



Scale-Full Size

FIG 23

As wear proceeds table and specimen move upwards producing a "depth of scar" reading on a micrometer dial gauge.

The oil under test drips at a controlled rate on to the wheel from a funnel above it. Times are read from a stopclock.

Test Procedure

During the investigations the following operating factors were used.

Oil drip to the wheel was maintained at three drops per minute. The load was 30 lbs.. The one inch diameter wheel was of hardened steel, Brinell number 507, ground and honed. A constant surface finish was ensured by rubbing before each test with the same grade of fine emery cloth (grade 00). A speed of 200 r.p.m. was used.

Two types of bearing metals were used. Preliminary tests of bearing metals were used. Preliminary tests were made with a tin base metal, then subsequently a lead base metal was employed.

Before using the machine it was necessary the wheel should be set as true as possible, as wear readings were made to the nearest 0.0001 inch. Any eccentricity resulted in oscillations of the micrometer dial gauge pointer. This was best achieved by varying the relative positions of wheel and spindle to find that of least eccentricity. Traversing the breadth of the wheel with various positions of the bearing metal specimen to find the best position further eliminated oscillation.

On starting a test the specimen of bearing metal was clamped

in position. A feeler gauge was placed between it and the stationary wheel and the load applied. The dial gauge was set to zero less the feeler thickness, to ensure that the gauge read zero when the load was first applied to the specimen.

With the speed above 200 r.p.m. oil was allowed to drip, the stop clock started, the load carefully applied, to prevent deformation of the bearing metal, and the speed adjusted to 200 r.p.m.. Wear was initially rapid and measurements were recorded frequently (every five minutes). Later in the test it was sufficient to take readings every quarter hour and then every half hour. Wear finally ceased and the test stopped. At the end of a test the length of scar on the bearing metal was measured.

Interpretation of Results

If the depth of scar is plotted to a base of time of test curves of the types shown in Figures 26 & 27 are obtained. A measure of rate of wear is given by the slope of the curve at a particular point. As shown the rate is initially rapid, becoming less and finally ceasing. It may be assumed that initially there is dry friction due to the small area and hence high pressure between wheel and bearing metal. This is followed by boundary lubrication, quasi-hydrodynamic lubrication, and finally, hydrodynamic lubrication. In the latter the pressure becomes sufficiently low not to rupture the oil film.

This pressure is referred to as the "critical" or "equilibrium" film pressure and is the maximum pressure which the particular oil used will support under the running conditions of the test.

Connelly has used volume instead of depth as a measure of wear, but the curves obtained have essentially the same characteristics.

From the geometry of the cylindrical scar formed in the test an expression relating its length l to it depth h is given by

$$l = 2\sqrt{dh - h^2}$$

where d is the diameter of the wheel. If the force between wheel and bearing meatl specimen is F, the width of specimen b, then the pressure at any depth P is given by

$$P = \frac{F}{2b\sqrt{dh - h^2}}$$

This equation is used for calculating critical film pressures when wear ceases.

The effect of using different bearing metals is illustrated by results given later.

Softer lead base metals give higher rates of wear than tin base, and therefore they have been chosen for all but the preliminary tests. They do suffer, however, from some flow of the metal.

Thomson, Scott, Ferguson and McBroom (46) show that when different loads are used displacement of the wear curves is obtained. The rate of wear varies with the load, butthe critical film pressure remains the same. The same authors show that oils of higher viscosity give lower rates of wear and higher critical pressures but as is shown by the results obtained on this investigation, viscosity is not the only important property of the oil.

Wear Tests

Analyses of the oil samples oxidised in the standard oxidation apparatus and used in the Avery-Brownsdon machine are given in Tables 5 and 6.

Preliminary wear tests, of the type described, using a tin base bearing meatal are given in Figures 26 and 27, the oils used being samples 2 and 3. Following this, in Figures 28 to 32, is a more detailed series in which a lead base bearing metal was employed. Samples 4, 5, 6 and 7 were used and 16 oxidised from 0 to 24 hours.

It is evident from the figures that oxidation causes a decrease in both the rate and amount of wear produced in the test. Sample number 5 shows particularly high changes and the exceptional nature of this low aromatic oil has already been pointed out. At this stage there is, however, no indication of

a correlation with standard oxidation test results (Table 9), nor oil analysis. Sample number 16 with high aromatic content and poor oxidation test results can be seen to give curves of similar type to sample number 4.

The results for all oils are collected together in Figure 33. Critical pressures are plotted to a base of time of oxidation, and an unexpected result is obtained. It can be seen that the graphs which are linear, show a rate increase which is of the same order for all samples.

Again, sampl e number 5 shows exceptional characteristics. The rate of increase is high up to nine hours when it then assumes a normal slope. Sample 16 has no exceptional characteristics.

Classical lubrication theory indicates that when speed is constant the pressure at which hydrodynamic conditions begin is proportional to the viscosity. Examination of critical pressures for the unoxidised oils however, does not verify this. This was also born out in the work of Thomson, Scott, Ferguson and McBroom (46) who, when using the same machine, with three oils of different viscosity obtained different values of Reynold's Number at the critical pressure. It would seem that in the present test that if factors such as wheel hardness, bearing metal, etc. are constant, the final pressure is a complex relationship of viscosity and oil constitution.

This would explain why sample number 16 gives a graph not differing greatly from the others, although the viscosity becomes very high on oxidation (the viscosity ratio is 8.4). The reason for similar rates is, however, less easily explained. It is known that certain compounds and chemical groups have a considerable effect on lubricating properties. The formation of such groups at rates which differ somewhat, but not to the extent of those responsible for high viscosities and residues, is possible. Their formation may be more dependent on physical conditions than oil constitution. If, as is probable, the responsible groups are intermediates in the oxidation process, then it must be assumed that the amount present in the oils approximately is proportional to time of oxidation.

Evidence to support this will be given later when an examination of the change in acidity with oxidation is made on the above samples.

It does not appear possible to relate these particular lubricating properties with the results obtained in the standard test.

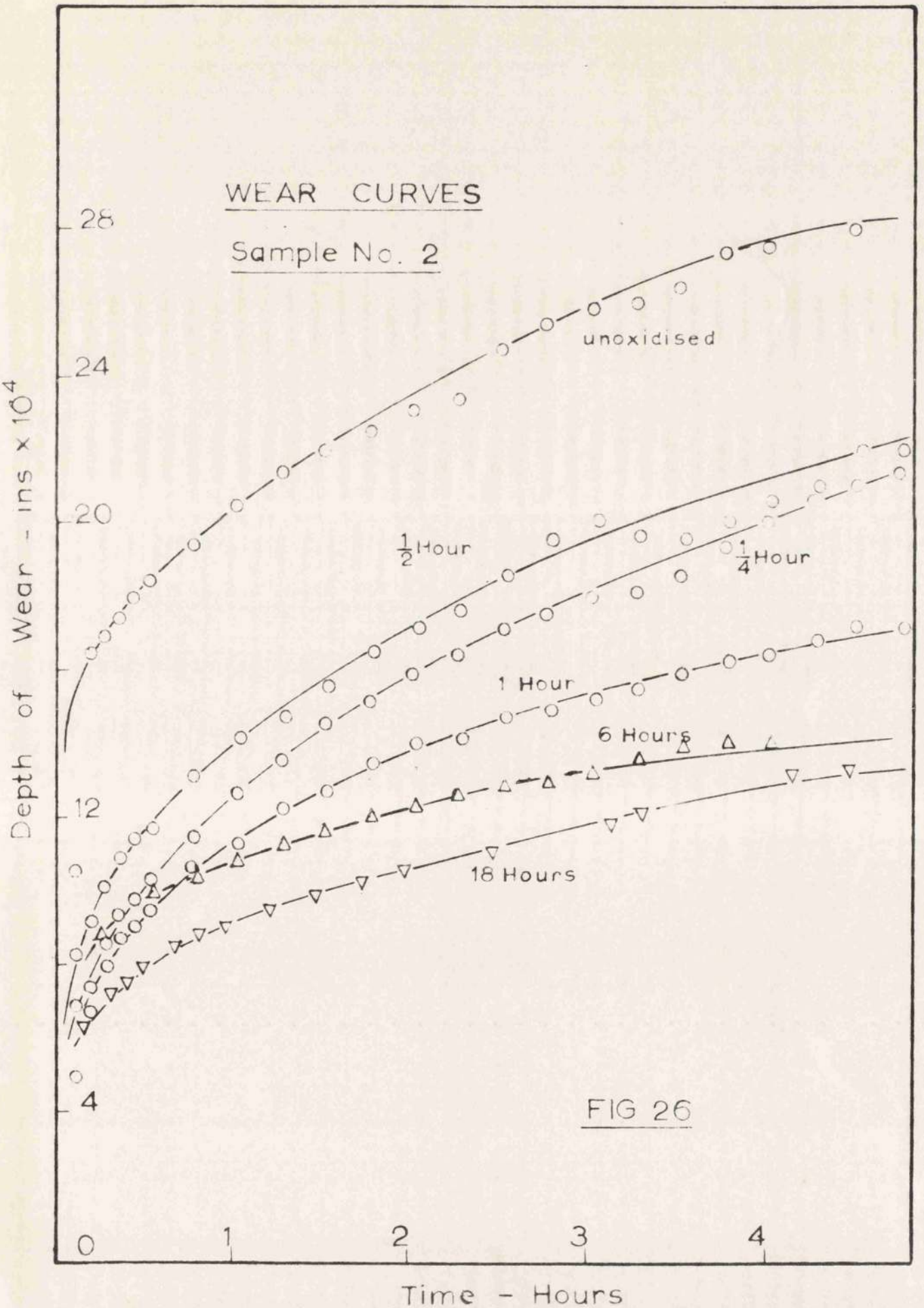

WEAR CURVES
Sample No. 2
28
24
20
12
4
unoxidised
½ Hour
¼ Hour
1 Hour
6 Hours
18 Hours
Depth of Wear - ins x 10⁴
0
1
2
3
4
Time - Hours

FIG 26

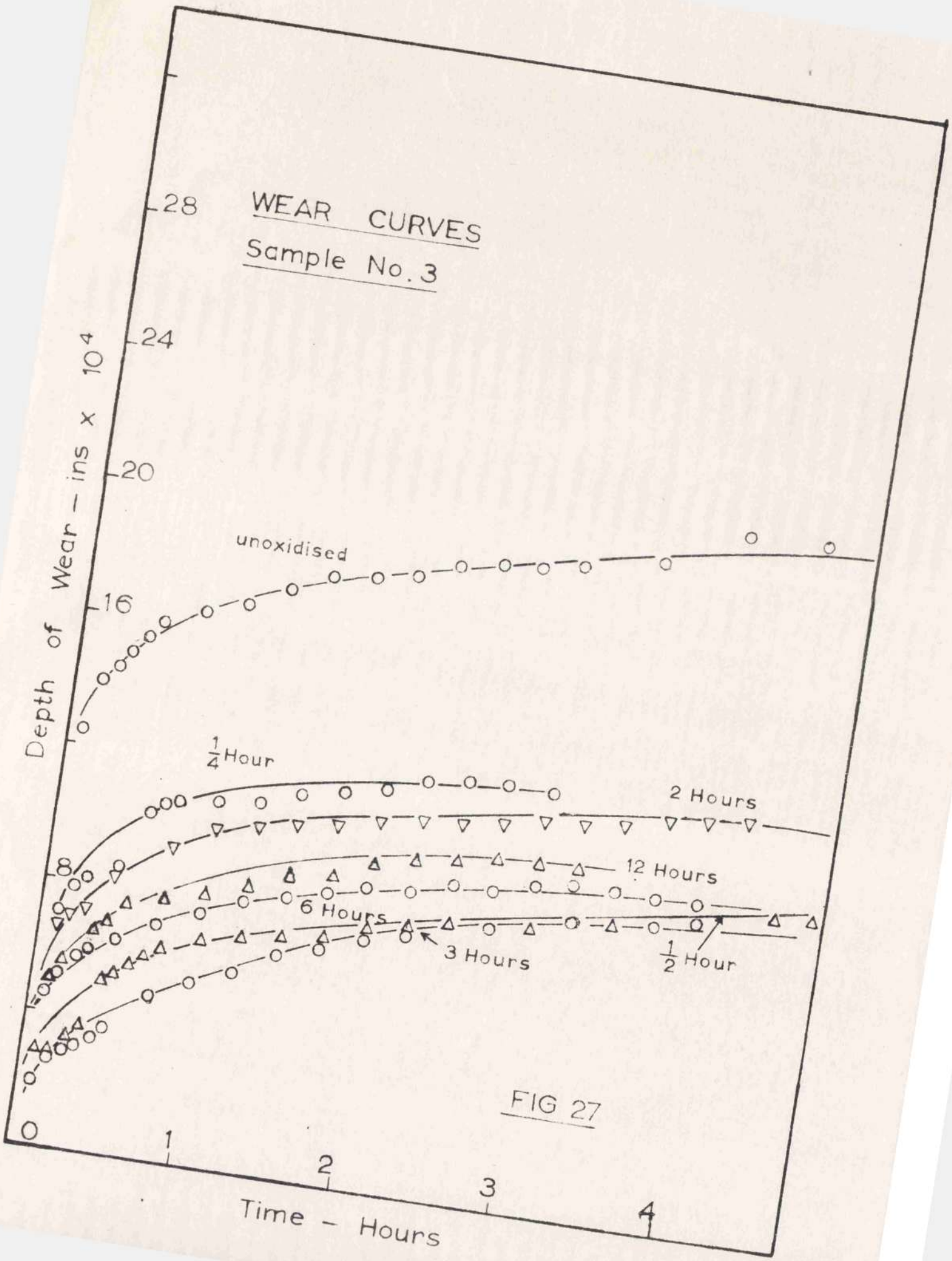
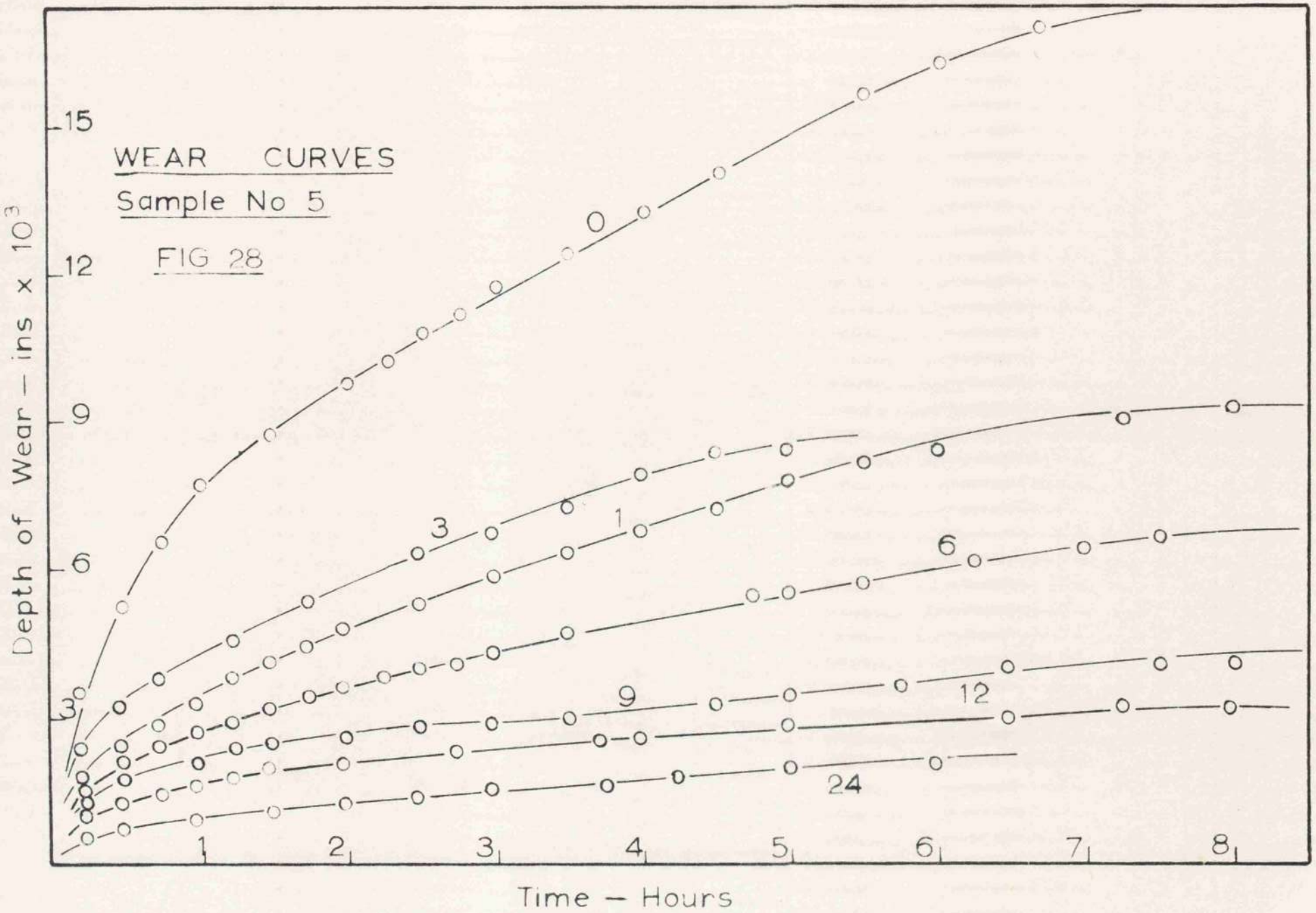

WEAR CURVES
Sample No. 3
Depth of Wear – ins x 10^4
28
24
20
16
8
0
unoxidised
$\frac{1}{4}$ Hour
2 Hours
12 Hours
6 Hours
3 Hours
$\frac{1}{2}$ Hour
1
2
3
4
Time – Hours

FIG 27


WEAR CURVES
Sample No 5
FIG 28
Depth of Wear – ins x 10^3
15
12
9
6
3
Time – Hours
1
2
3
4
5
6
7
8
0
1
3
6
9
12
24

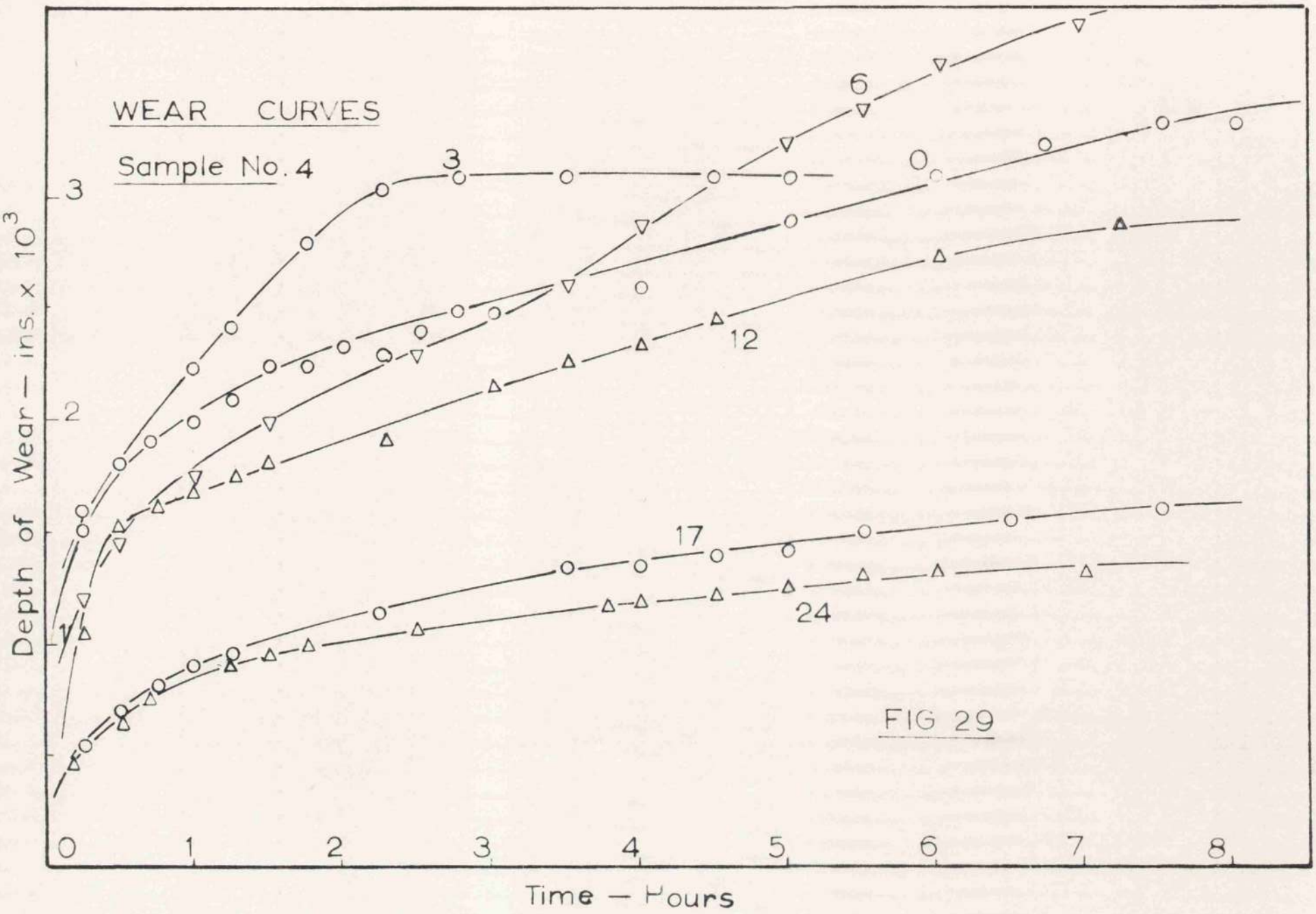

WEAR CURVES
Sample No. 4
Depth of Wear — ins. x 10^3
Time — Hours
0
1
2
3
4
5
6
7
8
1
2
3
6
0
12
17
24

FIG 29

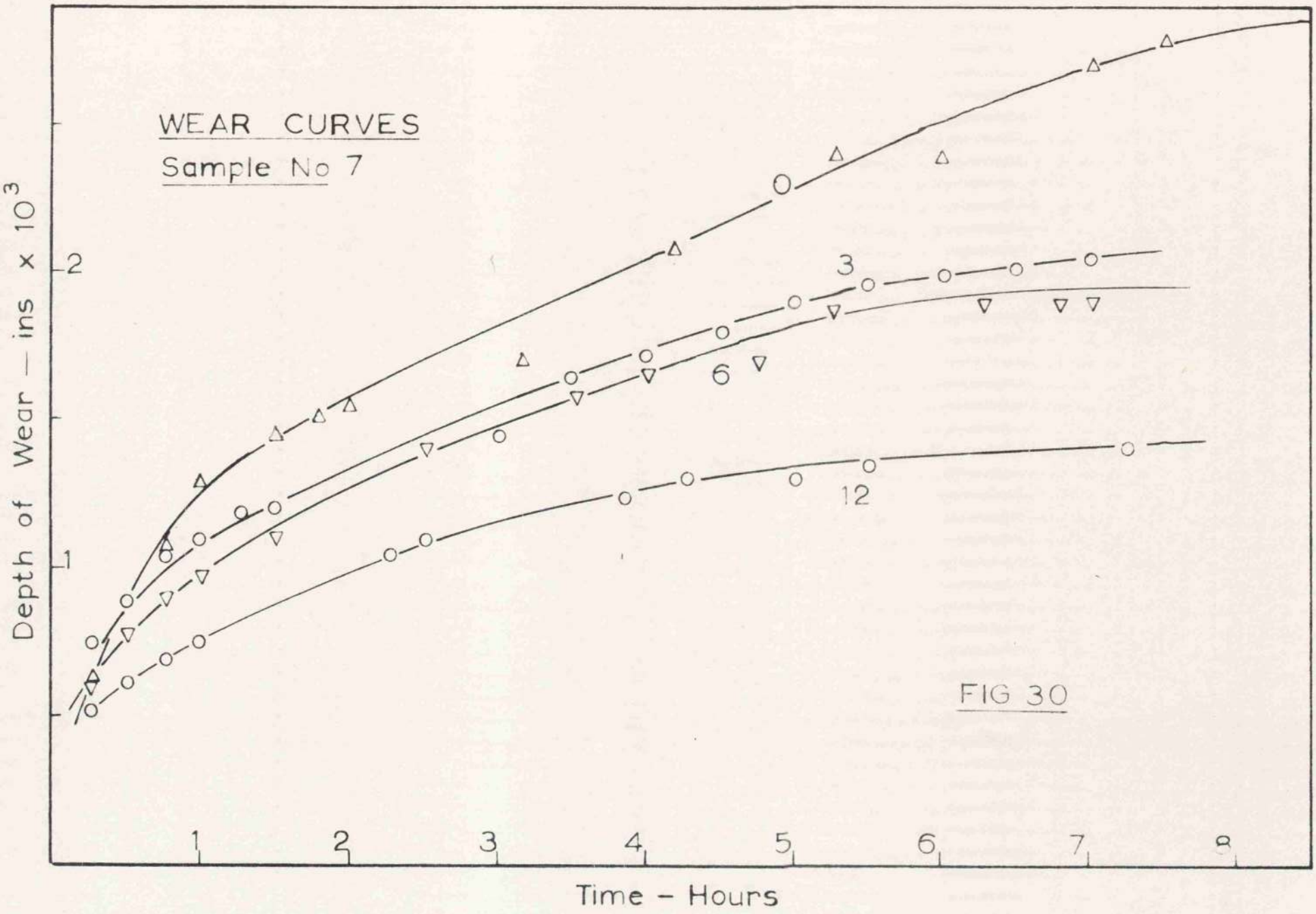

WEAR CURVES
Sample No 7
Depth of Wear — ins x 10^3
2
1
0
3
6
12
1
2
3
4
5
6
7
8
Time – Hours

FIG 30

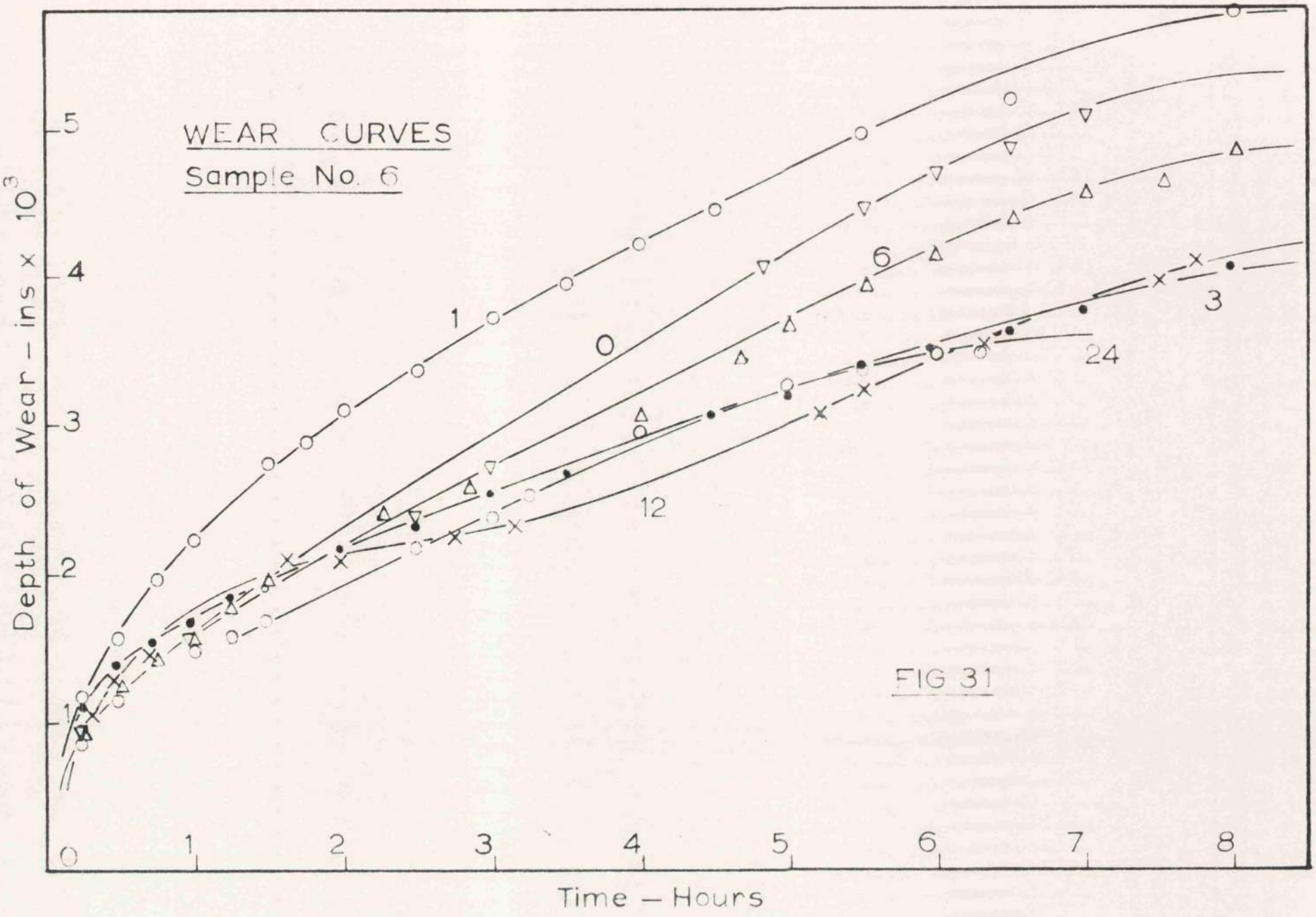
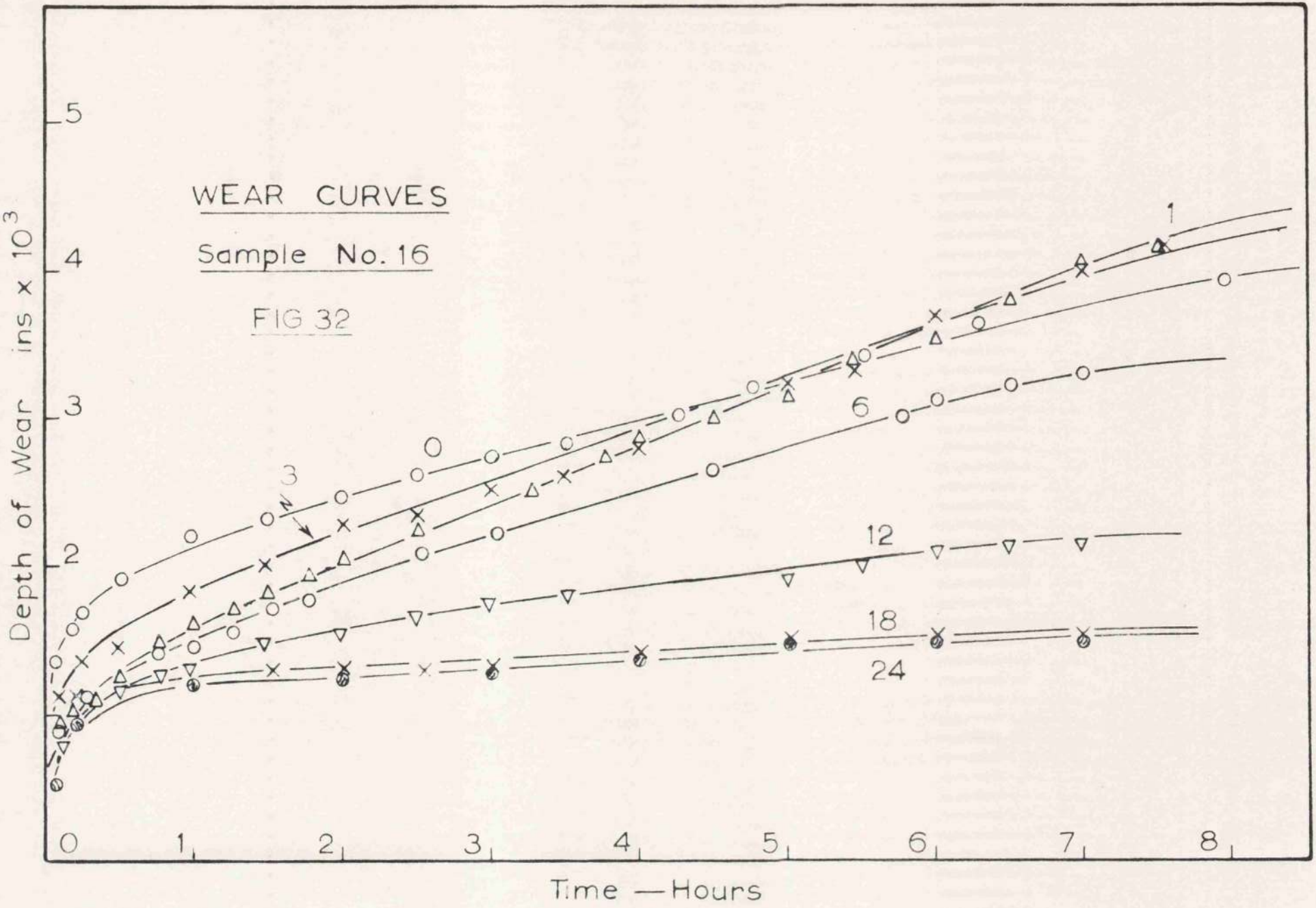

WEAR CURVES
Sample No. 6
Depth of Wear – ins x 10^3
Time – Hours
0
1
2
3
4
5
6
7
8
1
0
6
3
24
12

FIG 31


WEAR CURVES
Sample No. 16
FIG 32
Depth of Wear ins x 10^3
Time — Hours
0
1
2
3
4
5
6
7
8
1
3
6
12
18
24

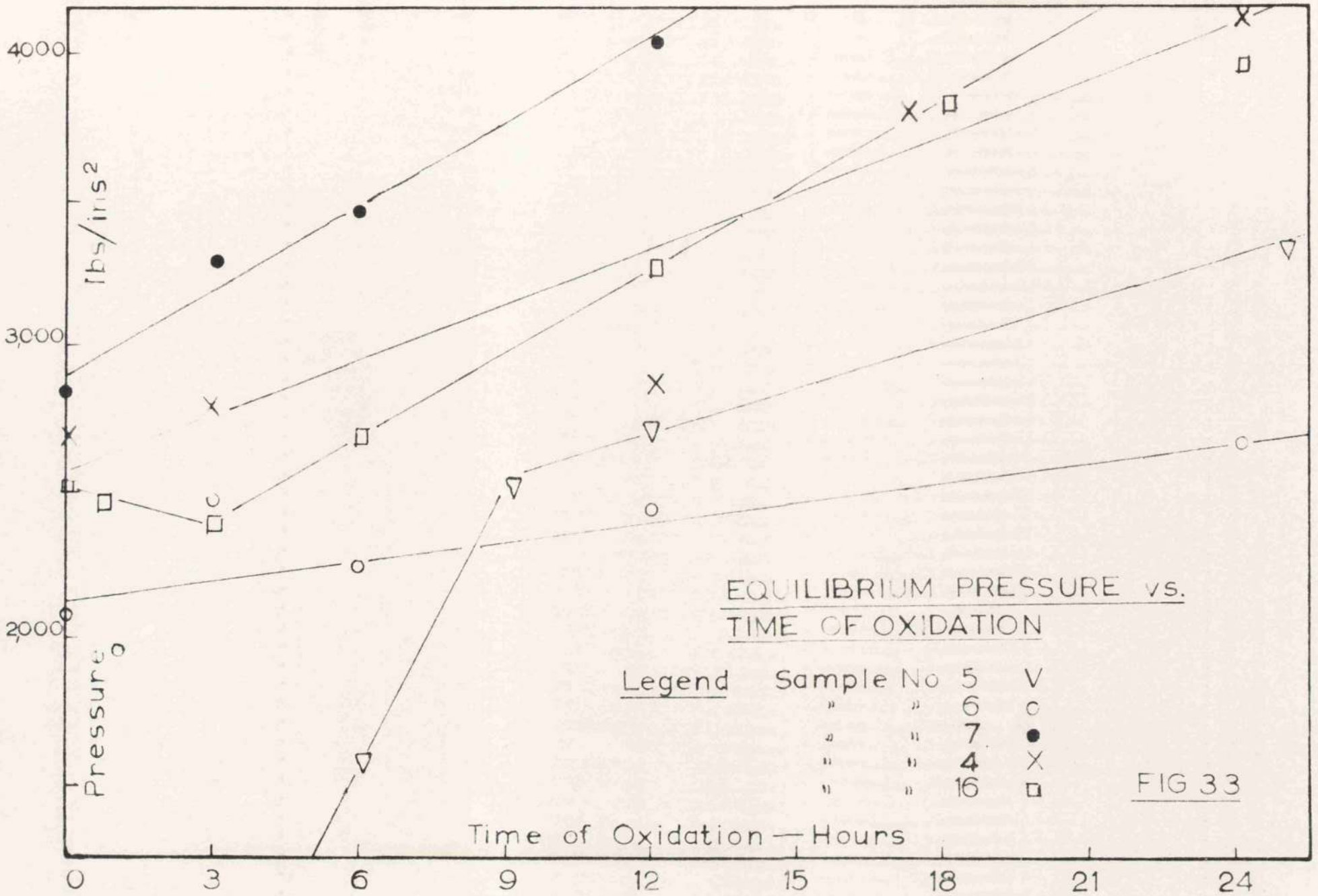

4000
3000
2000
lbs/ins²
Pressure
EQUILIBRIUM PRESSURE vs.
TIME OF OXIDATION
Legend
Sample No 5 V
" " 6 o
" " 7 ●
" " 4 X
" " 16 □
Time of Oxidation — Hours
0
3
6
9
12
15
18
21
24

FIG 33

The Four Ball Machine

The four ball machine is a standard apparatus used in research on lubricants. It is based on the original technique of Boerlage (47). Three ½ inch diameter hardened steel balls are clamped in the base of a cup containing lubricant. A similar fourth ball rotates at high speed on top of these. The balls form a pyramid structure with a known force pressing the two units together. Circular scars formed on the three bottom balls, at the points of contact, are measured optically. Arrangements also exist for measuring friction torques during running.

The contact conditions of the four ball test gives sliding motion under high pressure and therefore similates conditions in gears. It is thus useful for testing gear lubricants and E.P. additives, but much useful information may be derived by testing lubricating oil fractions.

Properties evaluated are load carrying capacity, protection against seizure, intensity of seizure, ability to restrict damage after seizure, and wear reducing and frictional characteristics of the oils tested.

A photograph of the Stanhope machine used in this work is given in Figure 25. The motor runs at a constant speed of 1375 r.p.m.. The driving spindle terminates in a chuck holding the top hardened steel ball, which rotates on top of the other

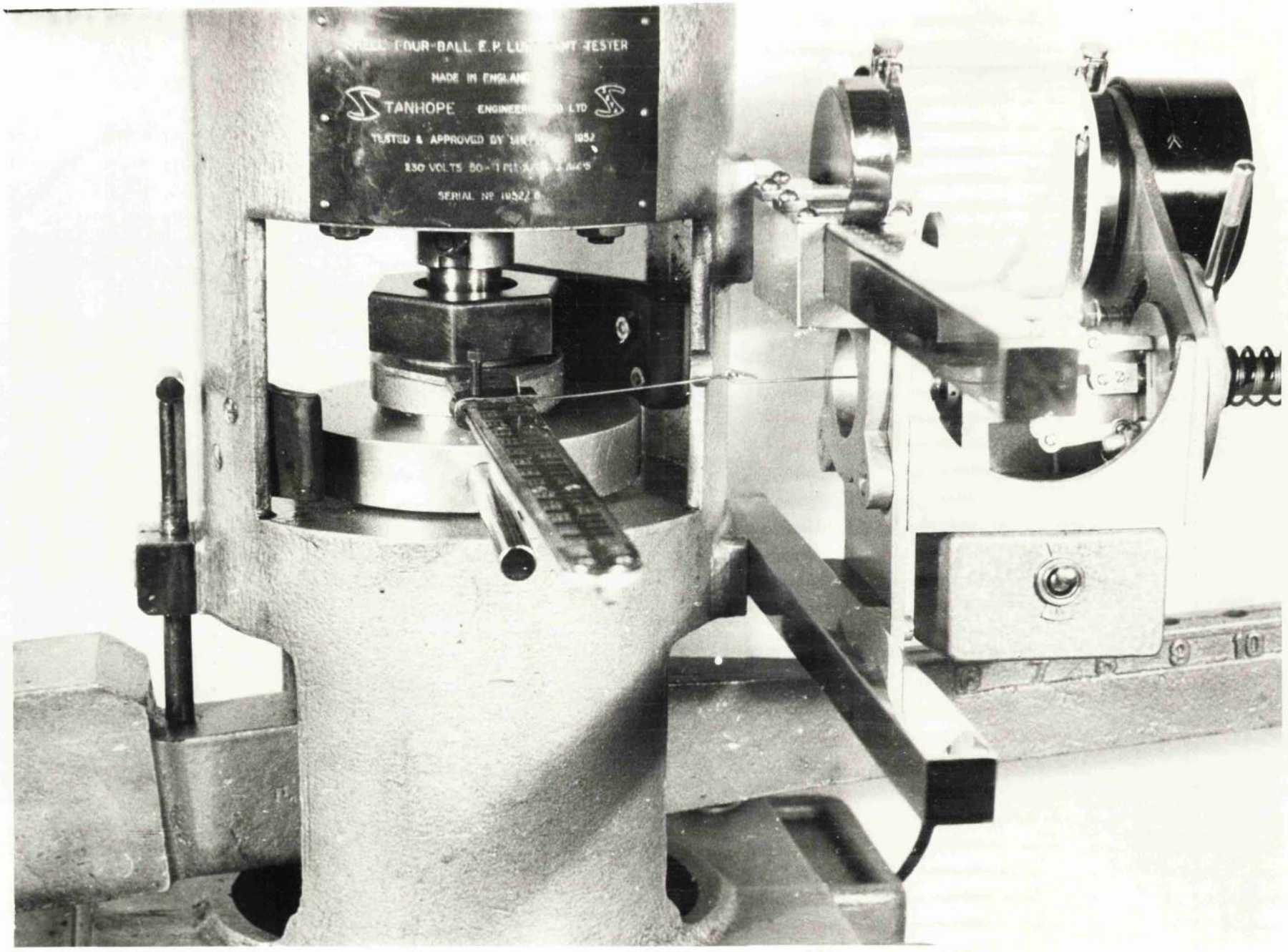

FOUR-BALL E.P.
TESTER
MADE IN ENGLAND
STANHOPE
TESTED & APPROVED BY
230 VOLTS
SERIAL
9
10

Fig 25

three, clamped in a steel cup by a ring and locking nut. The balls are covered with lubricant, about 8 ml. being required. The cup is mounted on a thrust bearing, consisting of a ball race, and permitting horizontal movement to ensure automatic centreing of top ball when theload is applied. Vertical displacemat of the bearing under the action of a loaded lever arm provides the entire force. Variations in load are obtained by weights suspended from various points on the arm. A locking device keeps the load in an "off" position until it is required.

Frictional torques are measured by an arm attached to the cup and a wire from this to a calibrated spring. Elongation of the spring is magnified and recorded on a rotating drum. The drum rotates once every 70 seconds to provide a continuous record of friction throughout the test.

Test Procedure

The motor is run unloaded for some minutes before testing to remove undue friction from the bearings. Four steel balls and cup are cleaned with light petroleum spirit and the three balls clamped in position. The fourth ball is slipped into the chuck and the cup filled with the sample to be tested.

A predetermined load is selected and is gently applied by removing the locking device.

The fourth ball automatically centres to give equal loads between the top and the other three balls.

A zero base line is drawn on the recording paper fixed to the drum which is then connected up. When the drum is revolving the test is carried out with the motor running for one minute. At the end of the test the three balls are removed from the cup, cleaned and the scar diameters measured by microscope. Each scar is measured in two perpendicular directions and a mean of the six readings taken.

A new set of balls is used for each load.

According to standard procedure, the cup should be filled with fresh sample for each load. As samples in the present work were small, this was not possible. A number of preliminary tests indicated that results were not affected by using the same oil for several loads.

Interpretation of Results

Table 17 shows a typical set of results for a four ball test. When the scar diameter is plotted on logarithmic co-ordinates to a base of load, curves of the type shown in Figure 26 are obtained. A line, the Herz line, represents diameter of indentation produced under a number of static loads. For low loads AB lies close to this. When point B is reached seizure of the metal takes place until an area sufficient to support this load under the oil film conditions is reached at C. After seizure a line CD increasing with load is obtained until point D is reached

SAMPLE - KUWAIT OXIDISED FOR SIX HOURS.

Applied Load-Kgs.	Three scars measured in two directions (given in mms.)						
	1	2	3	4	5	6	Mean
40	0.384	0.402	0.391	0.417	0.403	0.422	0.403
60	0.432	1.464	0.480	0.446	0.451	0.477	0.458
70(1)	0.535	0.516	0.495	0.480	0.540	0.518	0.514
70(2)	0.460	0.470	0.516	0.492	0.500	0.478	0.486
75(1)	0.493	0.508	0.509	0.522	0.522	0.512	0.511
75(3)	0.501	0.485	0.494	0.509	0.509	0.532	0.505
75(2)	2.075	1.925	1.948	1.870	2.220	2.035	2.012
80(1)	2.463	2.315	2.413	2.518	2.263	2.260	2.374
80(2)	2.383	2.180	2.484	2.358	2.298	2.160	2.313
90(1)	2.133	2.013	2.283	2.118	2.288	2.160	2.166
90(2)	2.330	2.250	2.300	2.115	2.418	2.303	2.286
100(1)	2.365	2.233	2.445	2.120	2.500	2.363	2.338
100	2.590	2.430	2.598	2.478	2.460	2.255	2.468
120	2.870	2.682	2.628	2.480	2.790	2.738	2.698
140	3.183	3.243	3.220	3.060	3.103	3.135	3.157
160	3.303	3.408	3.275	3.393	3.245	3.090	3.286
170	4.320	3.283	3.480	3.150	4.088	3.265	3.576
180(1)	3.208	3.473	3.348	3.388	3.338	3.463	3.370
180(2)	WELDED						

Table 18

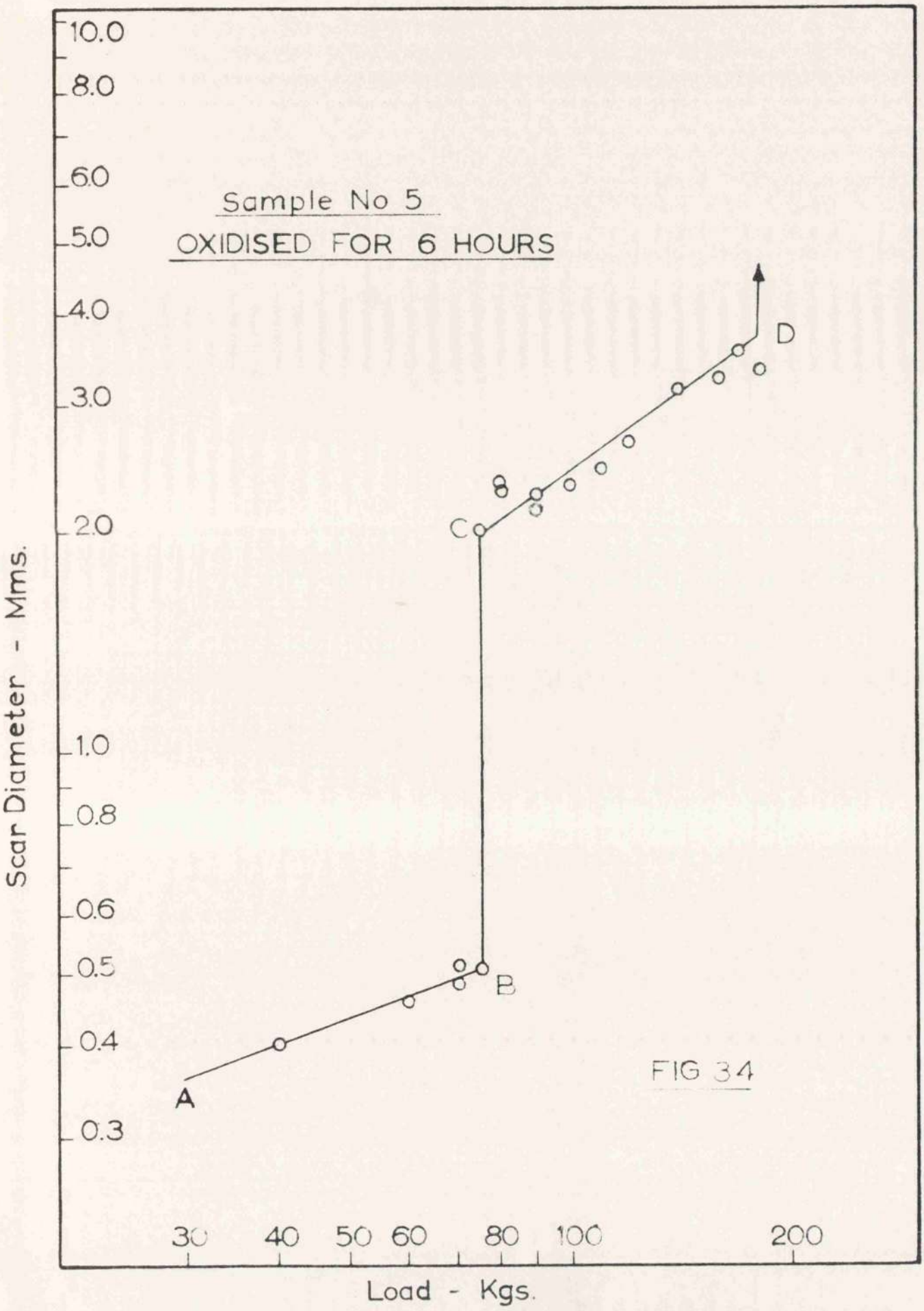

Sample No 5
OXIDISED FOR 6 HOURS
10.0
8.0
6.0
5.0
4.0
3.0
2.0
1.0
0.8
0.6
0.5
0.4
0.3
A
B
C
D
30
40
50
60
80
100
200
Load - Kgs.
Scar Diameter - Mms.

FIG 34

where the intensity of the heat generated is so great that the balls weld themselves together. The seizure load, weld load and general shape of the curve are factors used for comparing lubricants.

At loads below the seizure load relationship between the frictional torque and time shows a steady value. For loads equal to the seizure load, and above, the relationship is linear and of a low value. After a few seconds the onset of seizure causes very high torques which remain high until seizure is complete. The friction then drops to a steady value, but is still higher than it was before seizure took place.

The co-efficient of friction at any instant can be estimated from the force indicated on the friction trace. It can be shown that if the force indicated is F Kgs, the load P kgs and the arm of the torque L mms. Then the coefficient of friction f is given by

$$f = \frac{0.222FL}{P}$$

As already stated, there is a delay between the start of a test and the onset of seizure for loads above the seizure load. This delay is a measure of the effectiveness of a lubricant in preventingseizure. The factor is made specific, by estimating the load, which gives a delay of $2\frac{1}{2}$ seconds. This is found by plotting the seizure delay against a number of loads on logarithmic co-ordinates and interpolating.

From the resolution of the forces acting between the balls it can be shown that for a given load the mean specific pressure in Kg per square cm. is given by

$$\frac{51.4\ P}{d^2}$$

where d is the scar diameter in mms.

Four Ball Tests

Sample analyses of the oils oxidised for periods up to twenty-four hours and used here appear in Tables 5 and 6.

Complete tests on three series of oxidised oils were made. These are given in Figures 35, 36 and 37. Samples used represent a range of aromatics and are numbers 5, 4 and 16.

The welding load was found to vary significantly with the time of oxidation. Figure 38 shows this quantity plotted to a base of oxidation time. Welding loads were also measured on oxidised samples of oils numbers 6, 7 and 8.

A number of factors have been derived from the first mentioned figures and are given in Tables 19 and 20. These are (a) Seizure loads; (b) Seizure delay loads; (c) Coefficients of friction before and after seizure and (d) Scar diameters and pressures, immediately before and after seizure, and just before welding takes place.

Examination of Tables 19 and 20 in conjunction with Figures 35, 36 and 37 shows little change in the seizure load on

Time of Oxidation Hours	Weld Load Kgs.	Seizure Load Kgs.	Coeff. of Frict.		Seizure Delay Kgs.
			Before Seizure	After Seizure	
Sample No.4					
0	140	74	0.057	0.078	80
1	130	74	0.056	0.089	66
3	150	80	0.056	0.087	70
6	180	75	0.056	0.088	60
9	210	85	0.057	0.082	62
12	210	80	0.057	0.082	68
17	230	90	0.048	0.082	60
24	240	100	0.058	0.089	62
Sample No.5					
0	140	70	0.059	0.103	80
3	140	80	0.059	0.093	86
6	170	84	0.060	0.094	79
12	200	84	0.061	0.093	74
17	220	90	0.052	0.103	68
24	230	85	0.056	0.089	70
Sample No16					
0	150	50	0.023	0.094	50
1	170	50	0.022	0.092	52
3	240	55	0.027	0.091	58
6	280	50	0.023	0.076	61
12	280	70	0.038	0.104	43
18	320	85	0.027	0.103	49
24	360	90	0.022	0.120	?

Table 19

Time of Oxidation Hours	Scar Diams. in mms.			Pressures in Kg/cm^2		
	Before Seizure	After Seizure	on Welding	Before Seizure	After Seizure	on Welding
Sample No. 4						
0	0.45	1.85	3.0	18,700	1,110	800
1	0.50	2.00	3.1	15,200	950	683
3	0.52	2.00	3.3	15,200	1,030	708
6	0.51	1.97	3.7	14,800	990	676
9	0.51	1.98	3.9	16,800	1,110	711
12	0.48	1.95	3.3	17,800	1,080	992
17	0.50	2.00	3.5	18,500	1,030	966
24	0.65	1.90	3.4	12,100	1,420	1,068
Sample No. 5						
0	0.47	2.08	3.1	16,300	840	748
3	0.50	1.98	3.1	16,400	1,050	748
6	0.53	2.13	3.1	15,400	950	911
12	0.54	2.00	3.3	14,800	1,080	945
17	0.53	1.93	3.1	16,500	1,240	1,040
24	0.50	1.77	3.1	17,400	1,390	1,230
Sample No. 16						
0	0.35	1.50	3.00	21,100	1,400	856
1	0.37	1.38	2.96	18,600	1,360	993
3	0.38	1.40	3.24	19,700	1,450	1,175
6	0.38	1.30	3.20	17,900	1,520	1,400
12	0.50	1.57	2.70	14,400	1,460	1,975
18	0.60	1.37	3.15	12,200	2,330	1,665
24	0.61	1.26	3.12	12,500	2,900	1,890

Table 20

oxidation. Any tendency is for a slight increase and this is more noticeable with the high aromatic sample. Seizure delay shows a tendency to decrease.

Although varying from oil to oil, coefficients of friction show no significant change on oxidation.

Samples number 4 and 5 show little change in scar diameters immediately before and after seizure. However, sample 16 gives a definite increase before and a decrease after. Diameters at welding show little change on oxidation.

The above arbitrarily selected factors seem to be determined by the bulk of the sample, i.e. the average oil constitution, rather than by the presence of a relatively small amount of oxidised products. Those variations from oil to oil are greater than those brought about by oxidation. Due also to the scattered nature of these changes and their smallness, a correlation is not apparent wi th any measurement of oxidation.

When the pressures involved in the process are calculated from the applied loads and the corresponding scar diameters, the high aromatic sample in particular shows a definite change in pressure with load. Immediately before seizure there is a steady decrease and immediately after a corresponding increase. Similar changes are not shown by samples 4 and 5. All samples do, however, show an increase in pressure at welding due to an increase in welding load on oxidation.

If one considers the changes in all the factors tabulated in Tables 19 and 20, except welding load, caused by twelve hours oxidation, (the standard test time) these are found to be quite small even with the high aromatic oil and apparently cannot be correlated with the standard test.

In fact, it would appear only an accurate correlation based on an exact chemical analysis of the oxidation products would be feasible. Oil analysis, however, should provide some estimation of likely effects, e.g. low aromatic content, giving the types of change indicated.

The relationship between welding load and time of oxidation for six oils is shown in Figure 38. The increase in the load can be seen to be a minimum at the optimum aromatic content (about C_A = 10%), found in the absorption studies, but is not a function of the amount of oxygen absorbed. Sample number 5 with C_A = 3.3% shows an increase after twelve hours oxidation of 90 Kg, and an absorption of 1.5 litres of oxygen. Corresponding figures for sample number 16 are C_A = 45.2%, 220 Kg and 1.2 litres. The type of oxidation product formed must be important. Those of an aromatic nature provide considerably more protection against welding.

When the quantities measured in the standard oxidation test are compared with welding load, some correlation is evident.

With viscosity ratio and carbon residue increase there is a rapid initial increase in welding load. The rate of increase thereafter becomes less rapid. It would seem that those oxidation products which are effective in the standard oxidation test are also responsible for the increase in welding load. The lack of linear correlation, however, shows that the effect of the products in producing protection against welding tends to a limiting value as their concentrations increase. This would appear to indicate that the nature of the oxidation product rather than its concentration in the oil is important in preventing welding.

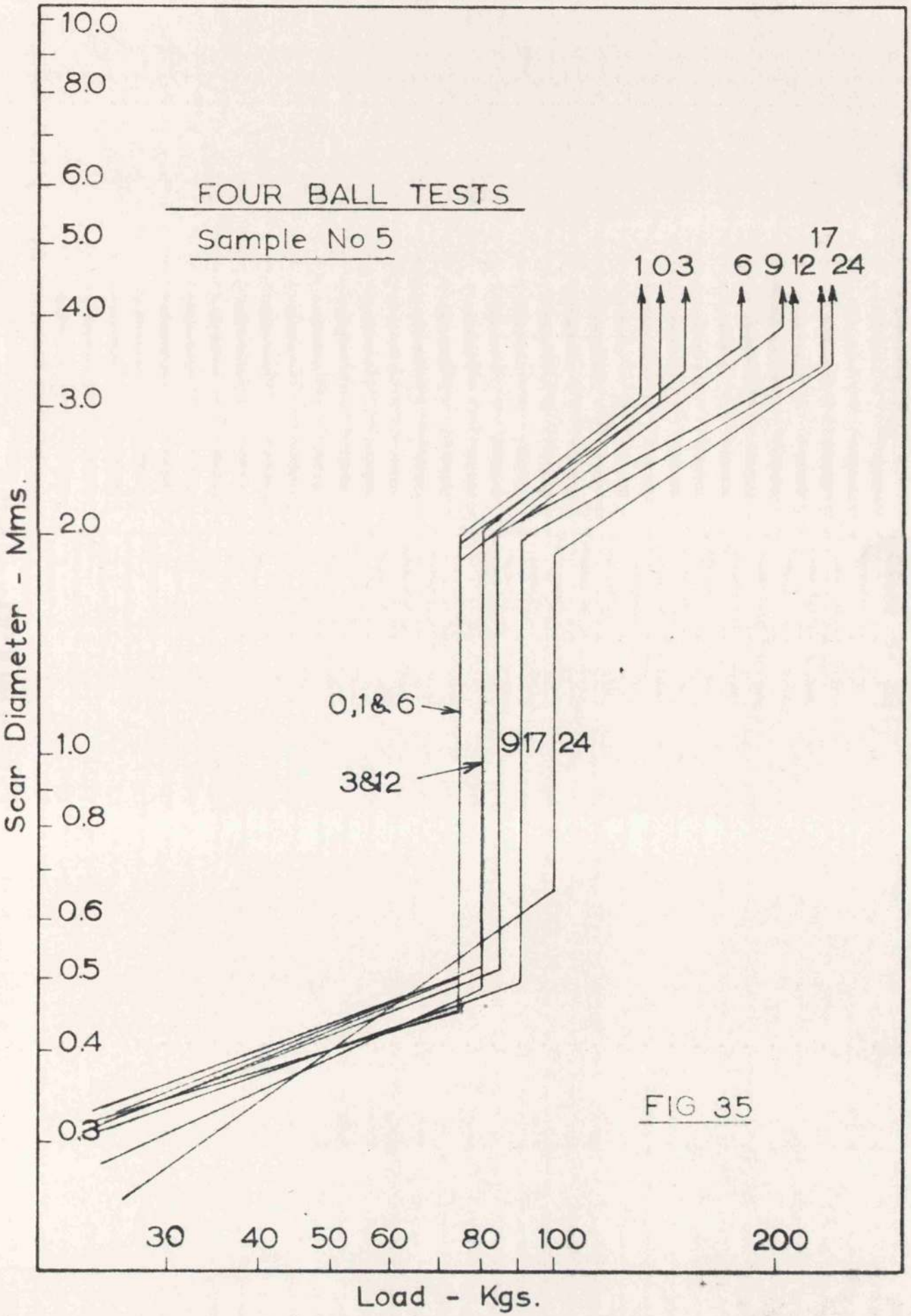

FOUR BALL TESTS
Sample No 5
10.0
8.0
6.0
5.0
4.0
3.0
2.0
1.0
0.8
0.6
0.5
0.4
0.3
Scar Diameter - Mms.
1 0 3 6 9 12 17 24
0,1 & 6
3&12
9 17 24
30 40 50 60 80 100 200
Load - Kgs.

FIG 35

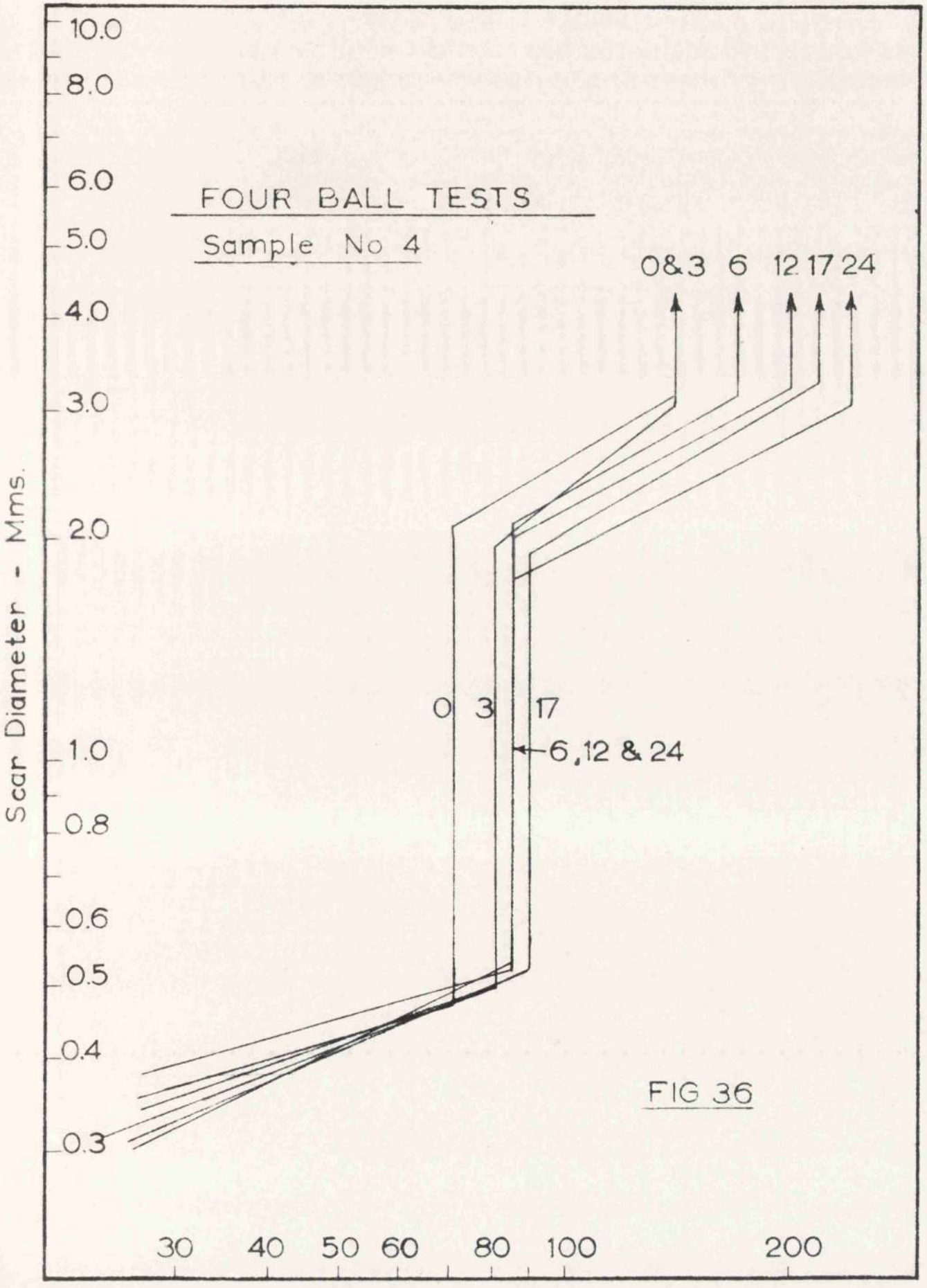

FOUR BALL TESTS
Sample No 4
0&3 6 12 17 24
0 3 17
6, 12 & 24
10.0
8.0
6.0
5.0
4.0
3.0
2.0
1.0
0.8
0.6
0.5
0.4
0.3
Scar Diameter - Mms.
30 40 50 60 80 100 200
Load - Kgs

FIG 36

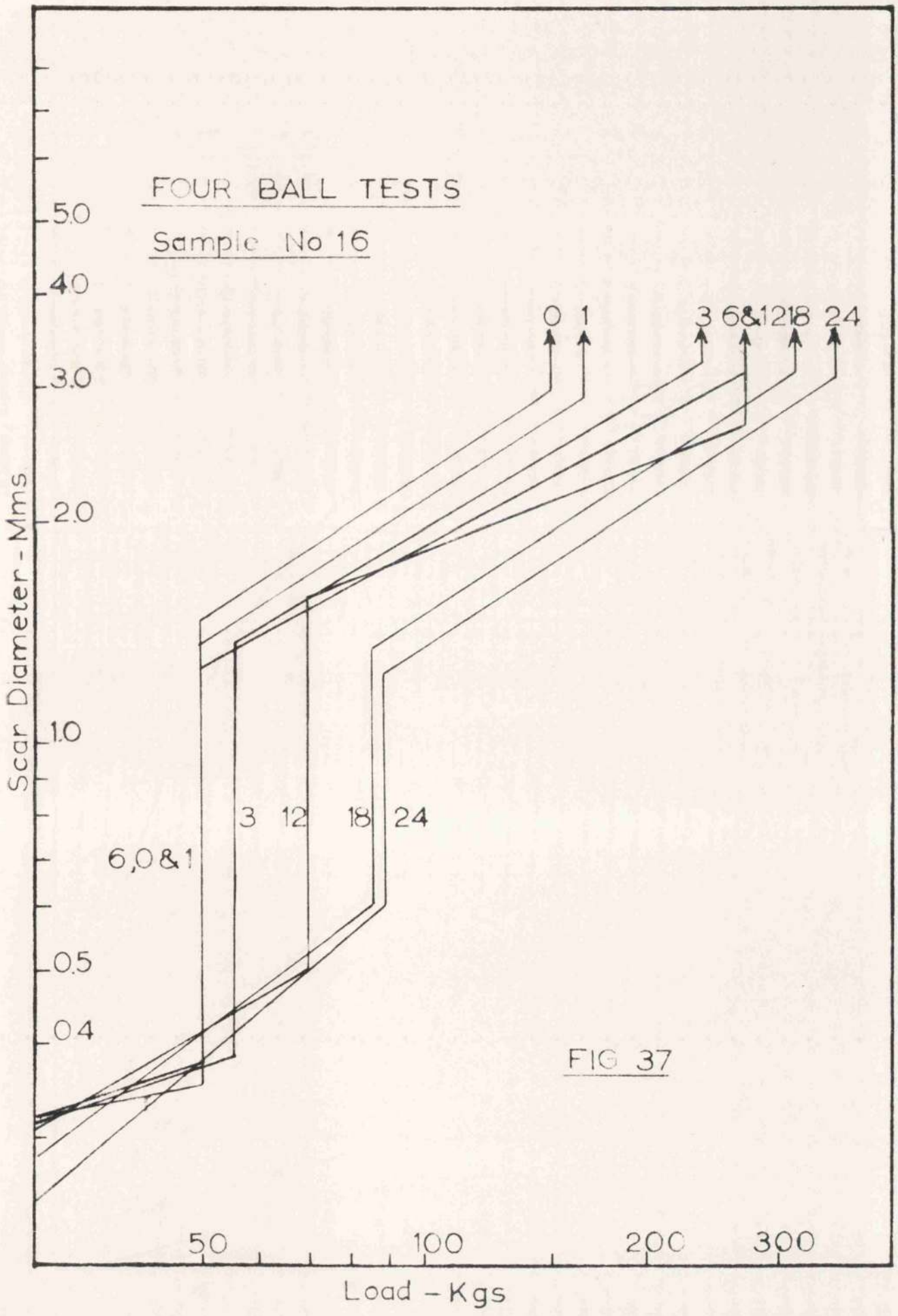
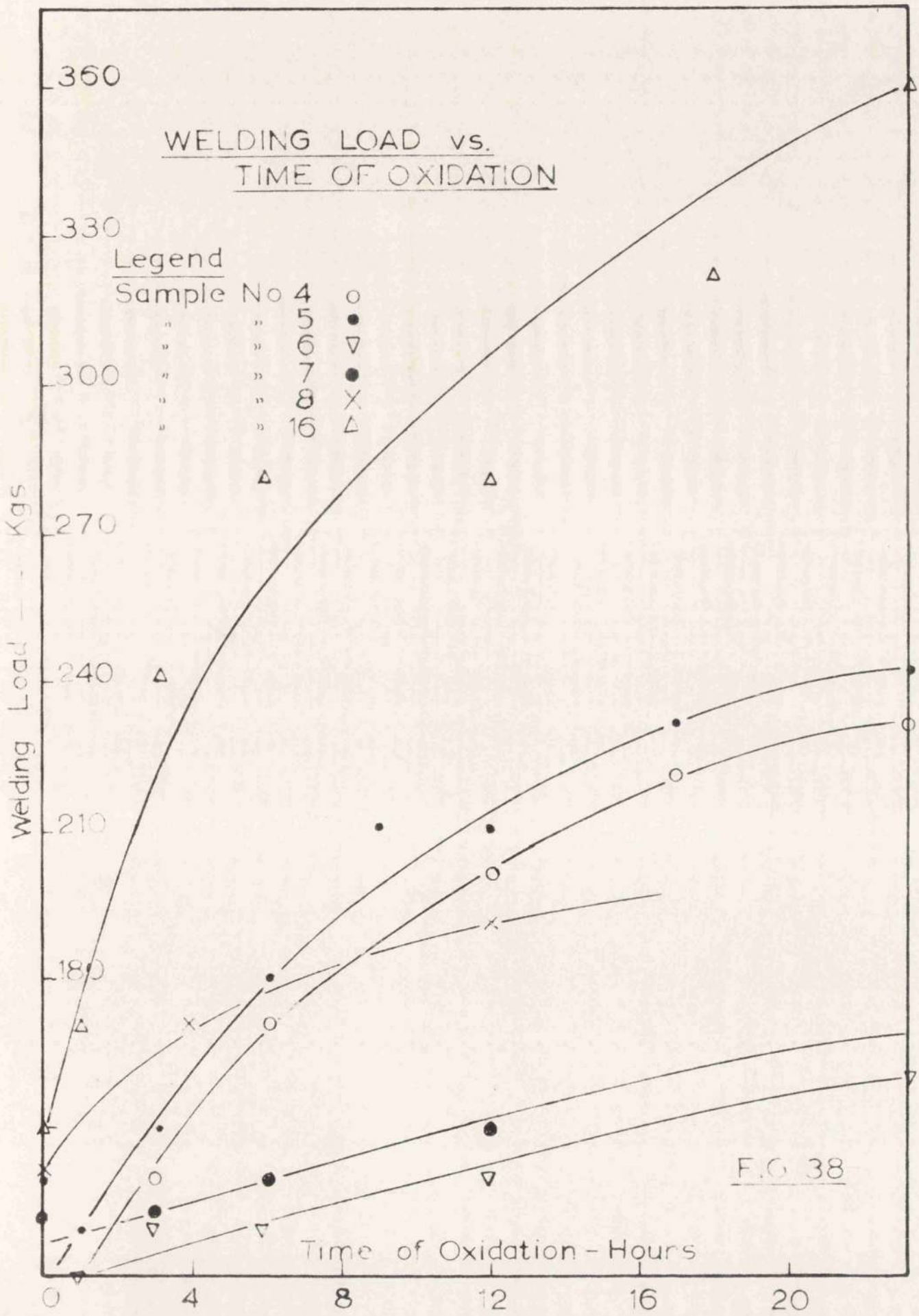

FOUR BALL TESTS
Sample No 16
5.0
4.0
3.0
2.0
1.0
0.5
0.4
Scar Diameter - Mms
0 1
3 6&12 18 24
6,0&1
3 12 18 24
50
100
200
300
Load - Kgs

FIG 37


WELDING LOAD vs.
TIME OF OXIDATION
Legend
Sample No 4 o
" " 5 •
" " 6 ▽
" " 7 ●
" " 8 X
" " 16 △
360
330
300
270
240
210
180
Welding Load — — Kgs
0
4
8
12
16
20
Time of Oxidation - Hours
F.G 38

The Measurement of Acidity in Oxidised Oils

The normal method of estimating acidity of oils with alcoholic potassium hydroxide is not suitable for oxidised samples. The dark colour obscures the colour change of the indicator.

End points in acid-alkali titrations can be determined by potentiometric means. A reference electrode of constant e.m.f. and an indicator electrode whose e.m.f. depends on the pH of the solution form a cell. When acid or alkali is added to the cell a measurement of potential difference between the electrodes gives a measure of the change in pH. Near the neutral point large differences occur with small additions of titrant. The end point is taken to be the point where the rate of change is greatest.

In the A.S.T.M. method for acidity in oil (48) an equal mixture of benzene and isopropyl alcohol containing 1% of water is used as solvent for the oil. A calomel electrode is the reference electrode (giving an e.m.f. of 0.242 volts on the hydrogen scale at 25°C) and a glass electrode the indicator. Measurements can be made on the pH scale (although they are not true pH values). These are plotted while additions of alcoholic potassium hydroxide are being made. A preselected pH value determined by a specially prepared buffer solution is taken as the end point.

The method is applicable to acids whose dissociation is greater than 10^{-9} and are soluble or nearly so in the solvent.

Experimental Technique

The electrodes are clamped in a 250 ml. beaker and connected to a suitable potentometer. The beaker is filled with a standard aqueous buffer solution of potassium acid pthalate (pH = 4) and the instrument standardised with this. Since total acidity is to be measured, the preselected end point for this is obtained by adding 10 ml. of buffer stock solution (27.8 gms. m-nitrophenol and 0.050 equivalents of potassium hydroxide in one litre iso-propyl alcohol) to 100 mls. of the solvent and measuring the pH.

Samples of oil varying from 20 to 1 gm. depending on the approximate acidity are dissolved in 125 mls. of solvent (50% benzene, 49% isopropyl alcohol and 1% water). As additions of 0.1N potassium hydroxide are added from a micro-burette pH readings are taken. Results are expressed as mgms. KOH per gm. oil. Using other buffer solutions measurements are also possible of strong acid number and strong and total base number. Complete details are given in the specification referred to.

Acidity Tests

Acidities were measured on samples numbered 4, 5, and 16 which had been oxidised for times up to twenty-four hours. The results are shown in Figure 39.

The aromatic oil which shows the highest rate of absorption of oxygen gives the greatest increase in acidity on oxidation. In fact a comparison of absorptions and acidities indicates that a similar amount of acid per unit volume of oxygen is formed in all samples. On average this is 3 mgms. KOH per gm. of oil per litre of oxygen. When the total volume of sample is considered it is seen that this quantity represents about 5% of the oxygen absorbed.

When previously the change in equilibrium or critical pressure with degree of oxidation (Figure 33) was considered it was found that small rates of increase of approximately the same order were obtained for all the oils tested. The results of the acidity measurements on the same oils might provide an explanation of this, if it is assumed that acidity is related to film pressure through the formation of metallic soaps on the bearing surfaces.

With sample number 5 there is an indication of a more rapid increase in acidity in the first six hours of oxidation when the critical pressure is also seen to rise more rapidly with time of oxidation. The high aromatic sample shows no exceptional

critical pressure changes while its acidity graph is intermediate in range. On the other hand, sample number 6 shows low acidity change and low critical pressure change. Thus, although the amount is relatively small, acidity would appear to be an important factor in deciding the effectiveness of the deteriorated oil, a fact that is not taken into consideration in the standard oxidation test. Since it seems to be related to the amount of oxygen absorbed it will, therefore, depend on the aromatic content of the oil, and hence aromatic content should give a reliable estimate of the amount of acid likely to be formed.

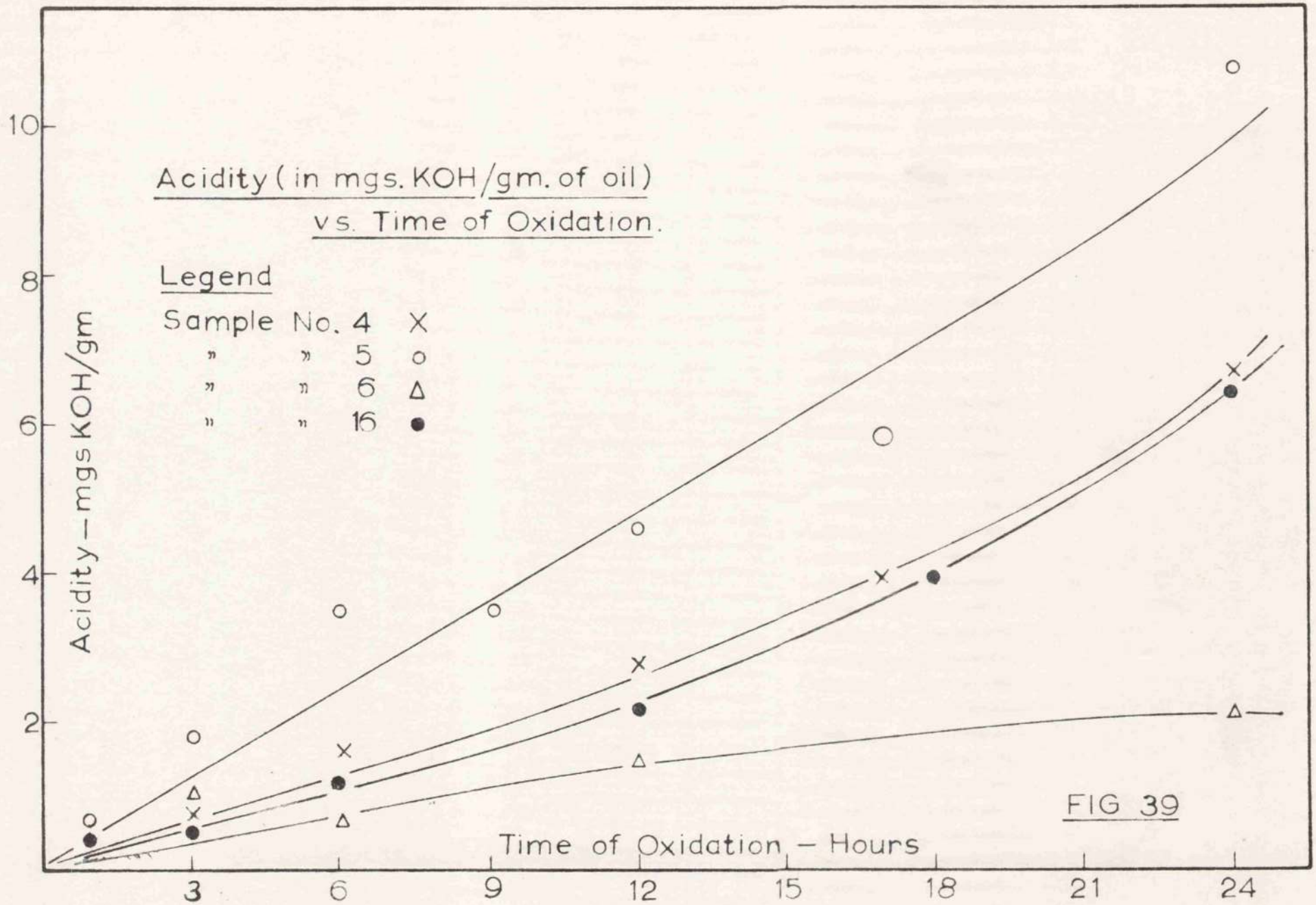

Acidity (in mgs. KOH/gm. of oil)
vs. Time of Oxidation.
Legend
Sample No. 4 X
" " 5 o
" " 6 Δ
" " 16 ●
Acidity – mgs KOH/gm
Time of Oxidation – Hours
0
2
4
6
8
10
3
6
9
12
15
18
21
24

FIG 39

Summary.

The aim of the present work has been an examination of the Standard Oxidation Test of the Institute of Petroleum for lubricating oils. Although it is known to give anomalous results the test is still used.

The investigation has been designed to show:

(i) the nature of oxidation test results on additive free mineral oils of known constitution and the possibility of predicting these from, and replacing the test with, an oil analysis,

(ii) the changes in a number of factors and the rates at which they take place during the time of oxidation,

(iii) if the above changes can be explained in terms of oil constitution and if the results obtained in the test give an indication of the nature of likely changes on oxidation.

It has been hoped to provide data enabling deterioration in the standard test to be compared with deterioration by other methods.

Rapid analysis of oil fractions was necessary to fulfil the purpose of the investigation. The V_k -n -d method of Structural Group Analysis has been examined with a view to testing its accuracy against the n - d - M method and speeding up the process to make it suitable for routine testing.

For oils lying within the limits of the V_k -n -d method statistical examination shows no significant difference between methods except for the percentage of the carbon atoms in aromatic structure. The n - d - M method tends to give a higher result. However the difference on average is only 0.7 per cent and insignificant for practical purposes.

The limits of the V_k - n - d method are narrow. Examination of the possibility of extrapolation of the method shows that it is safe to use

the method where the viscosity of the oil examined is higher than the upper viscosity limit of the method. Where the refractive index is higher however extrapolation will lead to erroneous results. High refractive index indicates a high percentage of the carbon atoms in aromatic structure and it is shown that the equation for calculating this breaks down where the value is high.

By constructing suitable nomographs the methods of calculations in the V_k - n - d method of analysis have been speeded up.

When performed according to specification the standard oxidation test results depend on the aromaticity of the oil. Oils with less than 10 per cent of the carbon atoms in aromatic structure show little change in the two quantities (viscosity ratio and increase in carbon residue) measured in the test. Such variations as do occur seem to indicate the lower the percentage the more the change. With more than 10 per cent of the carbon atoms in aromatic structure changes are considerable. The increase in carbon residue can be plotted to a base of aromaticity. With viscosity ratio the relationship is not so simple. However when a series of samples varying aromatic content are prepared by progressive extraction of one high aromatic oil, viscosity ratio and aromaticity can be graphed.

It is seen above that there is an optimum aromatic content of 10 per cent carbon atoms in aromatic structure, where changes in the oil are at a minimum. Also the analysis of the oil is seen to give some indication of the results obtained in the standard test.

When the rate of absorption of oxygen from the air in the standard test is measured the optimum value of carbon in aromatic structure is

again seen. Above and below 10 per cent absorption is high and a mimimum at this value. Figures have been obtained showing the order of absorption. In the 12 hours of the test this is found to vary from 420 to 1640 ccs. at N.T.P. for the different oils used.

From absorption studies and standard oxidation tests carried out according to specification it has been reasoned that below the optimum aromaticity the attack by oxygen is on the saturated hydrocarbons and above on the aromatic. The change in a number of factors studied has been shown to be proportional to time of oxidation in the standard test apparatus. Examples of these are density, the logarithm of viscosity, carbon residue and absorption of oxygen. Towards the end of the thesis it is shown that critical film pressure and acidity of each sample is proportional to time of oxidation. This indicates that if the standard test has to be used the time could be reduced to six hours instead of 12 and comparable results would be obtained.

Investigations have been made to find how the lubricating properties of the oils studied change on oxidation. Wear and rate of wear change considerably, but there is no correlation between these and either analysis or the result obtained in the standard oxidation test. Critical film pressure - the highest pressure at which hydodynamic lubrication takes place - has been found to increase at similar rates for all samples on oxidation.

Four ball tests found little change in seizure load, seizure delay time and coefficient of friction, for the oils studied, on oxidation. These seem to depend more on the bulk of the oil than on the small quantities of oxidised products. Welding load on the other hand increased markedly

on oxidation. The amount of the increase is related to the aromatic content of the original oil in the same way as the oxidation test results, i.e. minimum effect noticed with optimum aromaticity.

The acidity of an oil is an important factor in its practical application as a lubricant. It has been found here that this increases almost linearly with time of oxidation, but the increase is not related to either the results of the standard oxidation test or the analysis. It is suggested that due to its importance it would be better to measure the increase in acidity rather than the viscosity ratio in the oxidation test.

For the measurement of changes on oxidation, in the standard oxidation test apparatus; oxidationsfrom one to 24 hours have been used. The test according to specification considers an oil oxidised for 12 hours. Below in a table is extracted the data for the more important changes after this time for oils of differing analysis.

In general the analysis of an oil gives some idea of the types of change which may be expected. It is possible to predict standard oxidation test results. However, in no case is there definite correlation between changes in the oil and the standard test result only. Where a relationship does appear a better one is always obtained with structural group analysis.

Modern commercial lubricants contain additives which influence oxidation. Future work might be directed to finding how oils of known analysis, containing known quantities of specific additives behave in the standard oxidation test. Behaviour in the test could then be related to

Sample No	Mol Wt.	Viscosity centistokes	C_A *	Visc Ratio	Increase in Carb. Res%	Absorption * after 12 hrs.	Critical Film Pressure *			Welding Load. *			Acidity
							Before	After 12 hrs.	Inc.	Before	After 12 hrs.	Inc.	
5	538	85·54	3·3	1·56	1·04	1520	160	2,500	2,340	140	200	60	4·6
10	396	23·61	3·7	1·77	1·53								
11	469	52·30	4·2	1·63	1·40								
12	550	133·2	4·2	1·14	0·74								
13	837	522·7	5·5	2·54	0·74								
4	533	110·8	6·2	1·41	0·99	780	2,600	2,700	100	140	210	70	2·7
1	397	34·45	6·5	1·69	1·33								
3	676	535·8	6·8	1·15	0·52								
6	328	22·8	8·7	1·22	0·42	600	2,100	2,400	300	110	140	30	1·2
7	525	102·5	8·9	1·22	0·61	520	2,800	4,000	1,200	130	150	20	
2	454	90·36	9·5	1·27	0·53								
8	476	223·4	13·0	1·42	1·09	400							
14	311	22·61	18·6	1·70	1·70								
15	366	1300	24·1	27·90	4·62								
9	410	225·4	25·2	3·18	3·24	820							
16	264	25·37	45·2	8·40	6·69	1240	2,500	3,200	700	150	280	130	2·1
17	339	587·3	52·8	34·00	9·26	1620							

* For units see text.

analysis and additive contant. A suitable approach would be to take a few - say four oils in the range low, optimum and high aromatic content andstudy each with different additive types.

The way in which an oil behaves in use is the final criterion in deciding its efficiency as a lubricant. There is no published information regarding this factor and the standard test. Where resources are available field tests performed alongside the types of tests described here should yield useful information.

It is unlikely that a method will ever become available for the complete molecular analysis of an oil but techniques will be developed which will approach this. As these are, then it will be necessary to study the changes in oils on oxidation and these analyses figures. There are many approaches to the problem but the present has the advantage of using equipment which in the main is not costly to construct.

BIBLIOGRAPHY

1. Van Nes, K., and van Westen, H.A., "Aspects of the Constitution of Mineral Oils" Amsterdam 1951.

2. Vlugter, J.C., Waterman, H.I. and van Westen, H.A., J. Inst. Petrol. Tech. 18,735 (1932), 21,661 (1935) and 25,678 (1939).

3. Boelhouwer, C., and Waterman H.I., J. Inst. Petroleum, 40,116 (1954).

4. Zuidema, H.H., "The Performance of Lubricating Oils" New York, Reinhold Publishing Corp., 1952.

5. Chavanne, G. and Bode, E., J.Am.Chem.Soc., 52,1609 (1930).

6. Dupont, P., and Chavanne, G., Bull.soc.chim. Belg., 42,537 (1933).

7. Stevens, H.N., J.Am.Chem.Soc., 48,1824 and 2920 (1926) and 50,2523 (1928).

8. Stevens, H.N. and Roduta, F.L., J.Am.Chem.Soc., 57,2380 (1935).

9. Dornte, R.W., Ind.Eng.Chem., 28,26, (1936).

10. Denison, G.H., Ind.Eng.Chem., 36,477 (1944).

11. Fenske, M.R., Stevenson, C.E., Lawson, N.D., Herbolsheimer, G., and Kock, E.F., Ind.Eng.Chem. 33,516 (1941).

12. Hicks-Bruun, M.M., Ritz, B.L., Ledley, R.E., and Bruun, J.H., Ind.Eng.Chem., 36,526 (1944).

13. Larsen, R.G., and Armfield, F.A., Ind.Eng.Chem., 35,581 (1943).

14. See 4.

15. Dornte, R.W., and Ferguson, C.V., Ind.Eng.Chem. 28,863 (1936).

16. Dornte, R.W., Ferguson, C.V., and Haskins, C.P., Ind.Eng. Chem., 28,1342 (1936).

17. Larsen, R.G., Thorpe, R.E., and Armfield, F.A., Ind.Eng. Chem., 34,183 (1942).

18. Von Fuchs, G.H., and Diamond., Ind.Eng.Chem. 34,927 (1942).

19. Balsbough, J.G., and Oncley., J.C., Ind.Eng.Chem. 31,318 (1939).

20. Hock, H., and Lang, S., Ber., 75B, 300 and 1051 (1942).

21. Chernozhukov, N.I., and Krein, S.E., J.Applied Chem. U.S.S.R.) 10,1435 (1937), (Chemical Abstracts, 32,1664 (1938)).

22. Denison, G.H., and Clayton, J.D., S.A.E. Journal, 53,264 (1945).

23. Exline, D.G., Kramer, W.E., and Bowman, J.R., J.Inst. Petroleum, 29,295 (1943).

24. King, E.O., Proc.Ray.Soc. (London) A139,447 (1933).

25. Garner, F.H., Kelly, C.I., and Taylor, J.L., World Petroleum Congress, 2,448 (1933).

26. Rogers, T.H., and Shoemaker, B.H., Ind.Eng.Chem.Anal., 6,49 (1934).

27. Lamb, G.G., Loane, C.M., and Gaynor, J.W., Ind.Eng.Chem.Anal. 13,317 (1941).

28. Sligh, T.S., Jr., Proc. A.S.T.M., 21 Part II, 964 (1924).

29. Waters, G.W., and Burnham, H.D., Ind.Eng.Chem., 36,263 (1944).

30. Maugey, H.C., S.A.E., World Automotive Congress Preprints (1939).

31. Talley, S.K., Larsen, R.G., and Webb, W.A., Am.Chem.Soc., Petroleum Div., Atlantic City Meeting Preprints (1941).

32. C.R.H. handbook (1946).

33. Albright, B.E., Nelson, F.L., and Raymond, L., Ind.Eng.Chem., 41,897 (1949).

34. Georgi, C.W., S.A.E., Journal, 51,52 (1943).

35. Boelhouwer, C., van Steenis, J., and Waterman, H.I., Fuel, Lond., 33,60 (1954).

36. Lipkin, M.R., Mills, I.W., Martin C.C., and Harvey, W.T., Anal.Chemi., 21,504 (1949).

37. Mair. B.J., Nat. Bur. Standards, 14,345 (1935)

38. Standard Methods for testing Petroleum and its Products, Institute of Petroleum, London.

39. Youngsberg, G.E., and Pucher, G.W., J. Biol. Chem., 61,741 (1924).

40. Findlay, A. "Practical Physical Chemistry", Longmans, Green and Co., 1954.

41. Booser, E.R., and Fenske, M.R., Ind.Eng.Chem., 44,1850 (1952).

42. Diamond, H., Kennedy, H.C., and Larsen, R.G., Ind. Eng. Chem. 41,495 (1949)

43. Brownsdon, H.W., J.Inst.Met., 58,15 (1936).

44. Jannin, M.L., Rev. Metall., 19,109 (1922).

45. Connelly, J.R., Trans.Amer.Soc.Mech.Eng. 57,35 (1935).

46. Thomson, A.S.T., Scott, A.W., Ferguson, W., and McBroom, H.L., Trans.Inst.Engineers and Shipbuilders in Scotland, 257 (1953).